Environmental Impacts of Biodiesel Produced from Wastewater Greases

A Thesis

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by

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Dedication

To my family and friends

for all of their love, support, and encouragement

Acknowledgement

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Abstract

Environmental Impacts of Biodiesel Produced from Wastewater Greases

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This thesis evaluates the technical, economic, and environmental impacts of producing biofuels from greases that accumulate in wastewater systems. The research in this thesis is accomplished through performing four tasks: (1) identification of the statistical variability in wastewater grease composition and its subsequent impact on biodiesel production capacity, (2) exploration of processing methods and their performance in meeting biodiesel fuel specifications, (3) evaluation of the environmental performance of biodiesel produced from wastewater grease feedstock, and (4) analysis of economic and environmental feasibility of producing biodiesel from wastewater greases.

The two wastewater greases investigated in this thesis are grease trap waste (GTW), which is collected at restaurants, and sewage scum grease (SSG), which is collected at wastewater resource recovery facilities (WRRFs). Because wastewater greases are heterogeneous, degraded, and contain large amounts of water, solids, and impurities, GTW and SSG require different chemistry and additional processing steps for biodiesel production compared to conventional biodiesel feedstocks. The composition variability and a variety of parameters including wastewater quality are assessed during a year-long longitudinal study of GTW and SSG. GTW is primarily composed of water and has low lipid content (4%); however, ambient settling of GTW produces a floating grease layer

that concentrates the lipids (34%). The average lipid content SSG (21%) is comparable to the float grease in GTW; however, SSG lipid content exhibits seasonal variability that is not observed in GTW. SSG has higher lipid content in cooler months (15-40%) and lower lipid content in warmer months (3-21%). Both GTW and SSG lipids have similar free fatty acid content (75%) affects the reaction pathways used for conversion into biodiesel. Technical feasibility of biodiesel production is assessed using a variety of reactors and distillation techniques. A major hurdle to producing biodiesel is reducing sulfur content to meet fuel specifications; approximately 56% of wastewater grease biofuel samples in this project contain between 15-30 ppm sulfur, and only 23% are below the required fuel specification of 15 ppm sulfur. Sulfur contents are shown to decrease throughout biodiesel production with an overall sulfur reduction of 75-96%.

This thesis presents life cycle assessment (LCA) and techno-economic analysis to determine the environmental impacts and economics of biodiesel produced from wastewater greases. A process model is used to incorporate experimental biodiesel processing results and to create an inventory of the materials and energy required for biodiesel production. Monte Carlo simulation is used to perform a sensitivity analysis utilizing the longitudinal study data for variability of composition and biodiesel plant capacities. LCA is used to compare the greenhouse gas emissions (GHG) of biodiesel production to current raw grease disposal (business as usual) and a variety of solid waste disposal facilities including anaerobic digestion, incineration, and landfilling. Each solid waste scenario produces biogenic fuels that are considered to displace an equal amount of an existing petroleum fuel; this replacement of the petroleum fuel is treated as a credit (negative value). The waste solid disposal is the highest contributor to GHG emissions

(20-40%, depending on lipid content). Multiple solid waste disposals facilities are also analyzed and showed that landfilling has the highest GHG, followed by incineration, and anaerobic digestion has the lowest GHG emissions. Biodiesel production from wastewater greases has the potential to lower GHG emissions by 20-75% compared to current methods of disposal of wastewater greases.

Chapter 1. Introduction

1.1. Background

Biodiesel is a renewable fuel that can be used directly in an engine or blended with petroleum diesel. Currently, biodiesel is produced from a variety of feedstocks including a variety of vegetable oils, animal fats, and waste greases. As part of the Energy Policy Act of 2005 and Energy Independence and Security Act of 2007, congress created the renewable fuel standard (RFS) that mandates the U.S. Environmental Production Agency (USEPA) to set renewable fuel production volumes (USEPA, 2015a). The U.S. Energy Information Administration (USEIA) provides monthly reports on U.S. biodiesel production by state and region through production surveys administered to U.S. biodiesel producers (USEIA, 2016a).

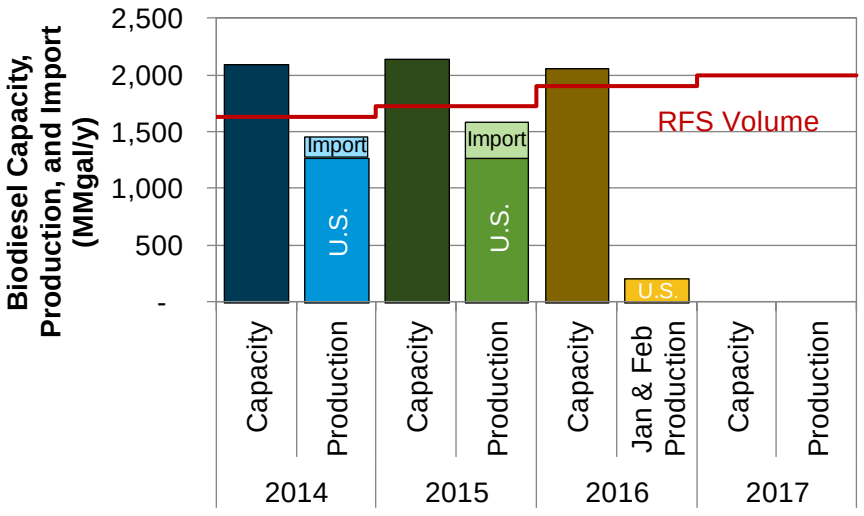


Figure 1.1: U.S. biodiesel capacity, production, and imports for 2014-2017. Data collected from USEPA renewable fuel standard (RFS) mandate (USEPA, 2015a), USEIA monthly biodiesel production report (USEIA, 2016a), and USEIA biodiesel import data (USEIA, 2016b).

Figure 1.1 displays the U.S. biodiesel capacity and production volumes (USEIA, 2016a), biodiesel import volumes (USEIA, 2016b), and the RFS biodiesel volume requirements (USEPA, 2015a). The U.S. has annually produced approximately 1.3 billion gallons of biodiesel (USEIA, 2016a) since 2014. The production of biodiesel in 2016 is on schedule to be larger than last year's domestic production. The 2016 two-month total (January and February) production is 210 million; this amount is 40% higher than the same two-month total in 2015.

Biodiesel feedstocks vary, but the majority of U.S. biodiesel was produced from vegetable oils, animal fats, and recycled materials in 2015 (Figure 1.2).

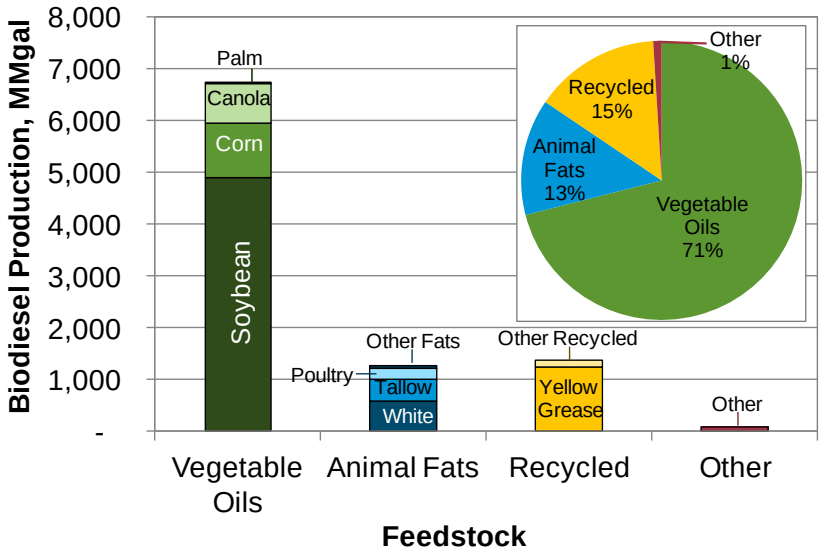


Figure 1.2: U.S. feedstock input for biodiesel production. Data collected from USEIA monthly biodiesel production report (USEIA, 2016a).

In 2015, 71% of the feedstock was from vegetable oils, 13% from animal fats, and 15% from recycled feeds (USEIA, 2016a). The two most prominent feedstocks were soybean

oil and yellow grease (waste cooking oil) which made up 52% and 13% of the total feedstock, respectively (USEIA, 2016a).

The Midwest region in the U.S. produced 85% of soybeans (USDA, 2015) and 73% of biodiesel (USEIA, 2016a) in 2014. USEIA uses Petroleum Administration for Defense Districts (PADD) as a geographical method for analyzing fuel production supply and movements in the U.S (USEIA, 2012). The districts are East Coast (PADD 1), Midwest (PADD 2), Gulf Coast (PADD 3), Rocky Mountain (PADD 4), and West Coast (PADD 5). These districts can also be used for examining regional biodiesel production. Figure 1.3 presents a map of the U.S. with PADD distinctions and biodiesel production by PADD.

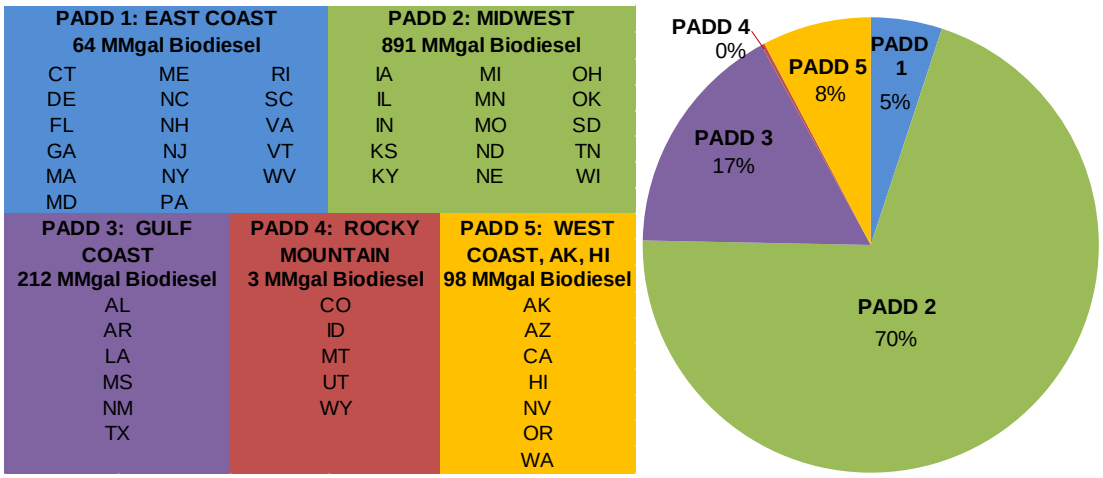


Figure 1.3: U.S. biodiesel production by petroleum administration for defense districts (PADD). PADD state abbreviations listed from USEIA (USEIA, 2012). Biodiesel production data collected from USEIA monthly biodiesel production reports (USEIA, 2016a).

PADD 2 was the highest consumer of on-highway distillate fuel at 12.5 billion gallons (USEIA, 2015b) and produced about 900 million gallons of biodiesel (USEIA,

2016a). If the biodiesel was blended with the on-highway distillate fuel, this would make about a 7% volume blend of biodiesel in petroleum diesel in PADD 2. PADD 1 was the second highest amount of on-highway distillate fuel at 10.7 billion gallons (USEIA, 2015b) and produced about 61.0 million gallons of biodiesel (USEIA, 2016a), which was only about a 1% volume blend with on-highway distillate.

While PADD 2 is abundant in land and soybean production, PADD 1 is abundant in population. The U.S. Census Bureau (USCB) estimated that 2012 population for PADD 1 was 117 million while PADD 2 was 82 million (USCB, 2016). Along with the size of populations in metropolitan areas, there is an abundance of waste materials from food and wastewater industries (Wiltsee, 1998). Therefore, using waste streams in populated regions could be beneficial in producing a local source of biodiesel rather than transporting fuel across the country. Wiltsee studied the amounts of waste cooking oil (WCO) and grease trap waste (GTW) produced across 30 U.S. metropolitan areas. These waste materials are referred as "recycled" materials mentioned in the monthly biodiesel production reports, which is the second largest feedstock for biodiesel production. WCO is the raw material collected from restaurants, filtered, and dewatered; the remaining fats, oils, and greases (FOG) are typically considered yellow grease. Wiltsee refers to yellow grease in the study, but based on his description this thesis will refer to it as WCO. GTW is kitchen effluent that is collected in a grease interceptor and is a combination of FOG (brown grease), floating solids, wastewater, and sediments.

Figure 1.4-A displays the amount of WCO and GTW that could annually be produced for the 30 metropolitan areas studied by Wiltsee. In the study, a population-based grease production rate (kg/y/person) was estimated. In Figure 1.4-A, this

population-based rate was multiplied by the population of the 30 metropolitan areas and converted to pounds to give an annual rate for every area (lb/y). Both WCO and GTW show positive correlations with regression coefficients of 0.901 and 0.694, respectively (Wiltsee, 1998).

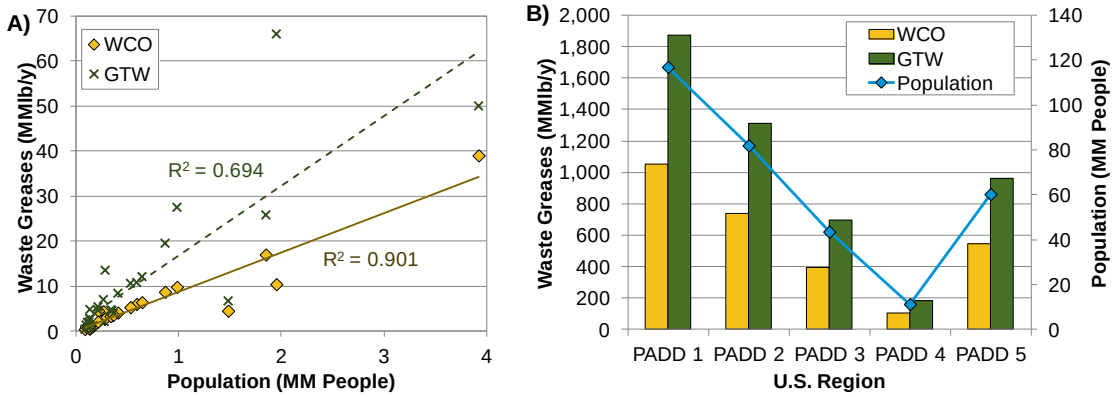


Figure 1.4: Waste grease feedstock production. (A) waste grease amount versus population from Wiltsee study (Wiltsee, 1998) (B) waste grease estimates and population by PADD.

Wiltsee also determined the weighted average of the population-based production rates of WCO and GTW were 9 lb/y/person and 16 lb/y/person, respectively (Wiltsee, 1998). These weighted averages were multiplied by the PADD population (blue line of Figure 1.4-B) to give an annual estimate of greases (bar chart Figure 1.4-B). The PADD population is represented by the blue line graph in. There is more GTW available, but this amount is the total quantity of the FOG, waste solids, and wastewater. The FOG, also known as brown grease, is a small portion of GTW and is the material that is converted to biodiesel. Alternatively, the WCO is the amount readily available for biodiesel production.

Yellow grease is converted to biodiesel by similar chemistry to pure vegetable oils and can be integrated fairly easily into current biodiesel production. Vegetable oils are an expensive feedstock and account for 70-88% of biodiesel production cost (Haas, McAloon, et al., 2005). WCO is a commodity in other industries, such as use as animal feed (Wiltsee, 1998), which can create competitive the feedstock costs. A benefit of GTW over other feedstocks is that producers of GTW must pay to dispose of the grease making it a negative feedstock cost to potential producers of biodiesel.

The research in this thesis is focused on producing biodiesel from wastewater greases such as grease trap waste (GTW) and sewage scum grease (SSG). GTW and SSG are underutilized, high-lipid waste streams that have the potential to be converted into biodiesel. These wastewater greases are a combination of FOG, water, and solids with highly variable composition (Ward, 2012; Wiltsee, 1998). The FOG, or brown grease, is the lipid portion of wastewater grease that can be extracted and converted into biodiesel. As previously mentioned, GTW is kitchen effluent that is collected in grease interceptors to avoid sewer blockages (Ragauskas et al., 2013). The quantity of lipids in GTW varies depending on the source and GTW management practice (Austic, 2010; Wiltsee, 1998) with a range of 0.1-40% lipid content (Canakci, 2007; Ward, 2012). In the United States, an estimated 1.8 billion kg/yr of lipids could be recovered from GTW (Ragauskas et al., 2013). SSG is floating material collected from settling tanks at wastewater resource recovery facilities (WRRFs). There is little literature specifically on SSG composition but extraction of brown grease into biodiesel has been performed (di Bitonto et al., 2016; Pastore et al., 2015). Some literature refers to SSG as black grease (Ward, 2012); however, this may also include sewage sludge which is the low-lipid

material found at the bottom of primary settling tanks. For the purpose of this thesis, the lipids extracted from both GTW and SSG will be referred to as brown grease.

Disposal methods of wastewater greases vary based on location and municipal regulations (Wiltsee, 1998). These waste greases are conventionally sent to a landfill or disposed through anaerobic digestion, incineration, or land application (Long et al., 2012; Wiltsee, 1998). Recovery of brown grease into a value-added product represents an opportunity to "recapture" and recycle waste streams from the food industry while reducing the processing burden of wastewater treatment and solid waste facilities.

The 100-year global warming potential (GWP_{100}) is a is a method to determine the potential climate change of long-lived greenhouse gases (GHG) over a 100 y time span (IPCC, 2013). For example, 1 g of methane (CH_4) is equal to 30 g of carbon dioxide (CO_2) which can also be expressed as 30 gCO_2eq. The fossil CO_2 arising from burning fossil fuels adds CO_2 to the atmosphere that has been sequestered for hundreds of millions of years; this could lead to an imbalance in the carbon cycle and a rising atmospheric CO_2 concentration. Alternatively, the CO_2 arising from burning a biogenic fuel adds CO_2 that has been recently sequestered in the biogenic source's lifetime, completing the carbon cycle. Therefore, the CO_2 produced from biogenic sources is considered zero because of the recent sequestration of carbon from the source into the atmosphere (Goedkoop et al., 2008; IPCC, 2013).

The degradation of organic material, such as in a landfill or anaerobic digester, emits biogas which is primarily composed of CH_4 (Jungbluth et al., 2007; Kabouris et al., 2009; Long et al., 2012; USEPA, 2015b), which accounts toward GHG emissions (IPCC, 2013). Landfill gas collection and anaerobic digestion offer ways to reduce the GHG

emissions from the CH_4 by flaring or cogenerating heat and electricity; the collection and use of this biogas can benefit waste disposal facilities while reducing GHG emissions. The extraction of the brown grease lipids for biodiesel production and anaerobic digestion of the wastewater has been reported to produce more usable energy than anaerobic digestion alone (Lopez et al., 2014; Tu & McDonnell, 2015). Separating brown grease lipids from GTW and SSG for biodiesel production has several potential benefits for waste management facilities, including reducing the volume of solid waste that is processed for disposal and replacing petroleum diesel combustion with a renewable fuel.

Life cycle assessment (LCA) is a systematic framework for examining the implications of products, processes, and activities, using specific metrics through life cycle impact assessment that approximate environmental damages (2006). The life cycle GHG emissions of low-sulfur diesel are approximately 93 g CO_2eq/MJ Fuel (Cai et al., 2013) while the life cycle GHG emissions for biodiesel produced from soybeans, animal fats, and WCO are 23, 24 and 18 g CO_2eq/MJ Fuel, respectively (Dufour & Iribarren, 2012; Huo et al., 2008). The biodiesel feedstock composition for 2015 was 71% vegetable oils, 13% animal fats, and 15% yellow grease, which has about 22 g CO_2eq/MJ Fuel life cycle GHG emissions. There was approximately a 76% reduction in GHG emissions for every MJ of biodiesel used compared to low-sulfur diesel.

The life cycle environmental impacts, including GHG emissions, for biodiesel produced from wastewater greases have been examined as a part of Chapter 4 and Chapter 5 of this thesis. The impacts are sensitive to the variability of the wastewater greases (primarily due to lipid content) and change depending on the waste solids

disposal method (Hums, Cairncross, et al., 2016; Hums, Olson, et al., 2016; Tu & McDonnell, 2015). The benefit of producing biodiesel from wastewater greases is the displacement of petroleum products which reduces the GHG emissions while creating a value-added product.

The research in this thesis was made possible through multiple collaborators whom offered not only their resources, but also industrial and research expertise in the wastewater grease and biodiesel fields. Russell Reid Waste Management (RRWM) is a grease hauler in the Philadelphia and New York metropolitan areas and provided GTW and a sampling location for the longitudinal study. Philadelphia Water Department (PWD) provided samples of SSG, performed fractionation experiments, and tested wastewater quality of SSG wastewater. The United States Department of Agriculture (USDA) Eastern Regional Resource Center allowed use of special equipment for biodiesel purification and analytical testing. Environmental Fuel Research (EFR), LLC is a business that was created to explore commercialization of biodiesel produced from wastewater greases. Part of the research for this thesis was performed as a research assistant for EFR, LLC and primary investigator during Phase I of an EPA Small Business Innovation Research (SBIR) grant.

1.2. Research Objectives

The purpose of this thesis is to determine the environmental impacts of biodiesel produced from wastewater greases through techno-economic analysis and life cycle assessment. The impact assessment is accomplished through the following objectives:

(1) Monitor the statistical variability in wastewater grease composition and its subsequent impact on biodiesel production capacity

(2) Investigate processing methods and their performance in meeting biodiesel fuel specifications

(3) Evaluate the environmental performance of biodiesel produced from wastewater grease feedstock

(4) Analyze the economic and environmental feasibility of producing biodiesel from wastewater greases

Each objective is organized into four chapters and summarized as follows.

1.2.1. Objective 1: Monitor the Statistical Variability in Wastewater Grease Composition

Presented in Chapter 2, objective 1 aims to understand the variability of GTW and SSG composition to determine the amount of brown grease, floating solids, wastewater, and sediments. This objective is accomplished through the following tasks:

(a) Collected and sampled GTW and SSG

(b) Performed fractionation of GTW and SSG

(c) Determined brown grease lipid quality

(d) Measured wastewater quality

(e) Examined correlations on data collected

Samples of GTW and SSG were collected approximately weekly for one year. GTW was collected at RRWM and SSG was collected by PWD. A grease lipid extraction (GLE) procedure was developed to fractionate the wastewater greases and determine the amount of brown grease, wastewater and solids. The brown grease was tested to determine its acidity and wastewater was tested to determine various wastewater quality metrics. The data collected were analyzed to determine correlations between parameters. These parameters included wastewater grease fractionated amounts,

wastewater quality testing, brown grease quality, ambient temperature, and precipitation. The data collected in this study were crucial for the sensitivity analysis in the economic and environmental impact assessment discussed in objectives 3 and 4 (Chapter 4 and Chapter 5).

1.2.2. Objective 2: Investigate Processing Biodiesel from Wastewater Greases

Presented in Chapter 3, objective 2 aims to investigate the processing methods and their performance for sulfur reduction and physical properties of biodiesel produced from wastewater. This is accomplished through the following tasks:

(a.) Convert brown grease from GTW and SSG into biodiesel

(b.) Purify biodiesel through washing and vacuum distillation

(c.) Analyze biodiesel yield and quality throughout each process stage

(d.) Identify correlations between sulfur content, yield, and distillation operating conditions

In this investigation, technical difficulties were identified throughout each production stage of biodiesel processing from wastewater greases. The production stages are identified in Figure 1.5. The biodiesel production from wastewater greases utilized in this research included the extraction of brown grease from GTW and SSG, conversion of brown grease to biodiesel, washing and drying of crude biodiesel, and distillation of crude biodiesel.

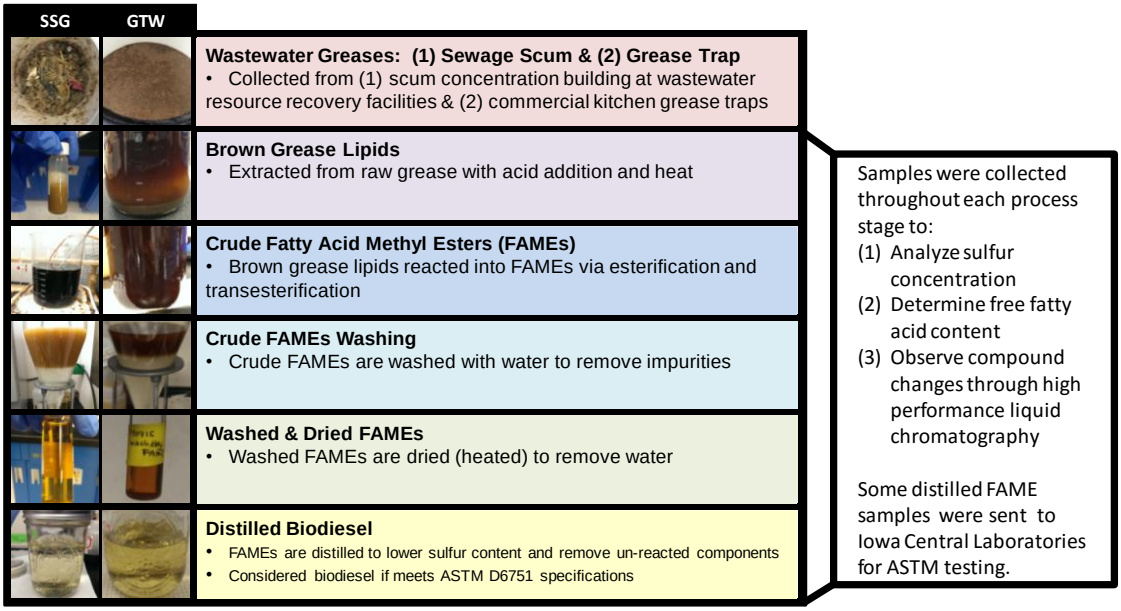


Figure 1.5: Biodiesel from sewage scum grease (SSG) and grease trap waste (GTW) process stages.

The analysis of each component throughout the process was necessary to identify complications due to the variability of the brown grease feedstock. High performance liquid chromatography (HPLC) was used to identify compounds in the process stage samples to observe the conversion of brown grease into biodiesel. The American Society for Testing and Materials (ASTM) standards ensure the quality of the product biodiesel (ASTM, 2015). Multiple distilled biodiesel samples were sent to Iowa Central Laboratories for the ASTM D6751 biodiesel standard; the biodiesel meets most of the requirements consistently except for the 15 ppm S specification. Therefore, the sulfur concentration was analyzed throughout biodiesel production and various distillation experiments were compared to compare operation conditions, yield, and sulfur content.

The research presented in this objective (Chapter 3) was performed using technology developed at Drexel University and EFR, LLC.

1.2.3. Objective 3: Evaluate the Environmental Performance of Biodiesel Produced from Wastewater Grease

Presented in Chapter 4, objective 3 aims to evaluate six environmental impacts associated with the production of biodiesel from GTW. This objective is accomplished through the following tasks:

(a.) Create a life cycle inventory of materials and utilities used in the biodiesel production from wastewater greases

(b.) Determine environmental impacts using life cycle inventory for 2-40% GTW lipid contents

(c.) Perform a sensitivity analysis to study the effect of lipid content on environmental impacts using Monte Carlo simulation

(d.) Compare environmental impacts of GTW biodiesel production to those of low-sulfur diesel, soybean biodiesel, and current GTW disposal

The stages of the life cycle inventory model included the collection of GTW from grease interceptors, extraction of brown grease, conversion to biodiesel, combustion of biodiesel in a vehicle and disposal of the biosolids to a landfill and wastewater treatment. Life cycle assessment (LCA) was used to quantify greenhouse gas emissions, fossil energy demand, and criteria air pollutant emissions for the GTW-biodiesel process. The sensitivity of lipid concentration in GTW was analyzed using Monte Carlo simulation and brown grease lipid content data collected during the longitudinal study. The life cycle environmental performance of GTW-biodiesel was compared to that of current GTW disposal, the soybean-biodiesel process, and low-sulfur diesel (LSD).

1.2.4. Objective 4: Analyze Economic and Environmental Feasibility of Producing Biofuel from Wastewater Greases

Presented in Chapter 5, objective 4, aims to analyze the economics and environmental impacts of biodiesel production from wastewater greases. This objective combined the findings of all the previous objectives to evaluate the economics and greenhouse gas emissions of producing biodiesel and co-product, biobunker, from both GTW and SSG. This objective is accomplished through the following tasks:

(a.) Research and incorporate multiple solid waste disposal options into a wastewater grease to biodiesel process model to create a life cycle inventory

(b.) Perform life cycle assessment and techno-economic analysis on base case scenarios GTW and SSG biodiesel production scenarios

(c.) Determine effects of raw grease composition through a sensitivity analysis on greenhouse gas (GHG) emissions and economics

A process model developed by EFR, LLC that analyzed biodiesel production from wastewater greases was used to determine the material and energy requirements for the life cycle inventory. The process model was expanded to include multiple solid waste disposal options to analyze their GHG emissions. This analysis also included a comparison of the GHG emissions of “biofuel production” and “business as usual” wastewater grease disposal as shown in Figure 1.6. Business as usual represented solid waste disposal including brown grease while the biofuel production extracted the brown grease to convert into biodiesel with a biobunker co-product and disposal of the remaining biosolids. Each disposal process included analyzing different biosolid disposal options at a landfill, anaerobic digester, or incinerator to identify the lowest GHG

emissions. The economics were also studied to determine an economically sustainable system based off of plant capacity and brown grease content.

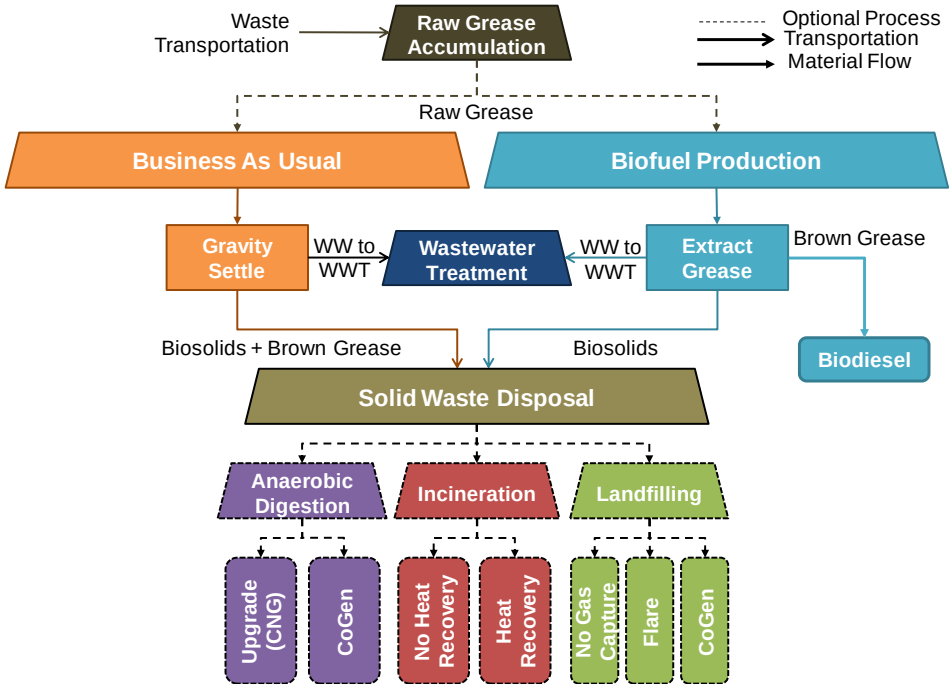


Figure 1.6: Wastewater grease disposal options. Comparison of business as usual to biofuel production with solid waste disposal choices of anaerobic digestion, incineration, or landfilling.

The longitudinal study composition data was used for a sensitivity analysis; the process model from Environmental Fuel Research, LLC was used to create a material and energy inventory; and the LCA of GTW revealed the need to examine multiple waste disposal options. Monte Carlo simulation was performed to determine the sensitivity of the wastewater grease compositions on the economics and GHG emissions for biofuel production.

Chapter 2. Longitudinal Study of Wastewater Grease Composition

2.1. Introduction

Grease trap waste (GTW) and sewage scum grease (SSG) are underutilized, low-quality waste streams that have the potential to be converted into biodiesel (Canakci, 2007; di Bitonto et al., 2016; Stacy et al., 2014). GTW is kitchen effluent that is collected in a grease interceptor. Grease hauling companies collect GTW from a variety of food service establishments and deliver the GTW to disposal sites. Frequently, smaller GTW loads are aggregated at transfer stations before being transported to disposal sites. SSG is floating material collected from settling tanks at water resource recovery facilities (WRRFs) where they are skimmed, partially-dewatered, neutralized with lime and transported to disposal sites. The disposal method for GTW and SSG varies depending on the region with common disposal at landfills, land application, anaerobic digesters, or incinerators (Long et al., 2012; Wiltsee, 1998). The lipids contained in GTW and SSG are often referred to as FOG (fats oils and greases) or brown grease; FOG can be separated from water and solids in GTW and SSG by heating and settling or by more advanced techniques such as solvent extraction. Brown grease lipid separation and conversion into biodiesel offers energy commodity benefits (Lopez et al., 2014) and possibly environmental benefits rather than disposal alone (Hums, Cairncross, et al., 2016; Tu & McDonnell, 2015).

The brown grease lipids that are extracted from these low-quality greases are highly variable in both quantity and composition (Long et al., 2012; Ward, 2012) which could impair the viability of a large-scale biodiesel production facility. Samples of GTW

have shown lipid content variability from 0.4-40% (Ward, 2012). To the authors' knowledge the lipid content of SSG is not as well researched but estimates of lipid composition between 3-11% have been measured (di Bitonto et al., 2016). The quality of the brown grease lipids also varies; these waste greases have high free fatty acid (FFA) contents which require different biodiesel conversion than conventional biodiesel feedstocks because of the formation of soaps (Ragauskas et al., 2013; Stacy et al., 2014). The FFA content of these greases ranges between 26-100% FFA (Ngo et al., 2011; Ragauskas et al., 2013). In addition, these greases have high concentrations of impurities including oxidized lipids, volatile organic compounds, nitrogen, sulfur, and metals (Ward, 2012).

This chapter presents results from longitudinal study that was performed to determine the composition of GTW and SSG in order to understand the variability and quality of brown grease lipids. The longitudinal study also included water quality testing of wastewater that was generated as part of the brown grease separation process and comparison to the quality of other wastewater streams within the wastewater resource recovery facility (WRRF).

2.2. Materials and Methods

The longitudinal study spanned a twelve-month period from July 2014 through June 2015. During this study, 61 samples of sewage scum grease (SSG) and 35 samples of grease trap waste (GTW) were collected on a roughly weekly basis and analyzed using a grease lipid extraction (GLE) process. GTW was sampled from Russell Reid Waste Management (RRWM), a grease hauler that collects a substantial portion of the GTW in

the Philadelphia metropolitan area, and SSG was sampled from three WRRFs in the Philadelphia Water Department (PWD) system.

2.2.1. Materials and Equipment

Sulfuric acid (Fischer Scientific), deionized water, methanol (Spectrum), toluene (Sigma-Aldrich), isopropanol (PTI Process Chemicals), potassium hydroxide (Sigma-Aldrich) were used in the separation and titration of the grease lipid extraction procedure.

A New Brunswick Gyrotory Water Bath Shaker G76 with Heater was used to heat and agitate the grease samples. A Clay Adams Dynac II Centrifuge was used to promote faster fractionation of grease layers.

Raw grease samples were collected and placed in 3.8 L (1 gal) UN-compliant shipping pails; the pails had a reusable locking lid and o-ring seal that enables transporting samples with minimal risk of spillage. The pails were stored in a 7 °C refrigerated storeroom between sampling and testing.

2.2.2. Raw Grease and Water Sampling

A schematic of the GTW and SSG sampling process is shown in Figure 2.1. Grease haulers collect GTW from the grease interceptors of multiple food service establishments (FSE). GTW readily separates into layers during storage because of the different densities of each layer. GTW samples were obtained from RRWM at their Deptford, NJ transfer station where an 1890 L (500 gal) polypropylene settling tank was located.

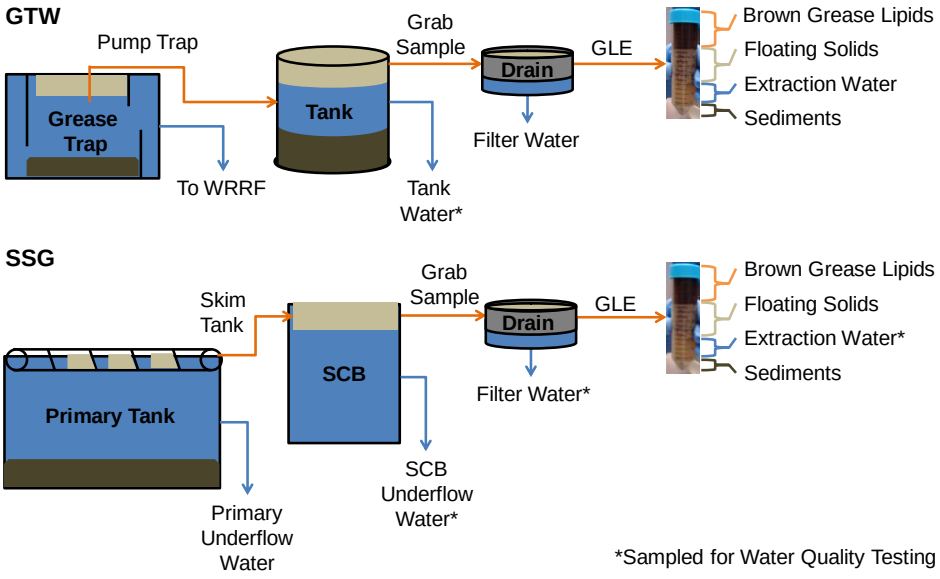


Figure 2.1: Schematic of sampling wastewater, grease trap waste, and sewage scum grease.

This settling tank received GTW from a box truck that conducted full pump-outs of interior and small exterior grease interceptors (removal of floating solids, wastewater, and sediments in the grease interceptor). Normally several loads of GTW were added to the settling tank before sampling, and the GTW would settle in the special tank for 1-7 days prior to sampling. Because the tank was made of polypropylene, the tank was semi-transparent; so it was possible to observe the transition between different layers. After settling, there were three layers visible in the tank: (1) a floating layer of grease, (2) a wastewater layer, and (3) a sediment layer (Figure 2.2). The floating solid and sediment layers were both darker than the secondary wastewater. The depth and volume of each layer was recorded prior to sampling from each layer for analysis.

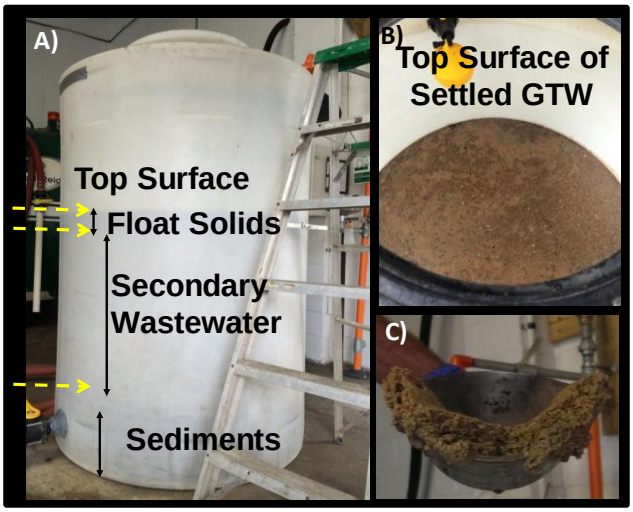


Figure 2.2: Grease Trap Waste Sampling. (A) Polypropylene tank showing defined layers; (B) Arial view of top surface; (C) Cross-section of floating solids after scooped from tank.

Samples from the top floating layer were obtained manually as grab samples. Occasionally, the floating grease layer appeared to be several separate layers of floating solids, liquid grease, and foam. When several floating layers were apparent, the layers were sampled separately. The samples from the top floating layer were analyzed by a grease lipid extraction (GLE) procedure developed for this project to identify the quantity of brown grease lipids, floating solids, extraction water, and sediments. A detailed description of the GLE process is discussed in Section 2.2.3. A sample of the wastewater layer (tank water) was obtained while the tank was drained.

SSG floats to the top of the primary settling tank at a WRRF. The surface of the primary settling tank is skimmed and the scum flows by gravity to a scum concentration building (SCB) where it accumulates and is partially dewatered by settling. Grab samples of SSG were collected from SCBs at PWD's three WRRFs. The SSG samples were collected from scum concentration buildings (SCB) at PWD's three locations.

Figure 2.3 displays photos of a scum concentration building and the process of obtaining SSG samples.

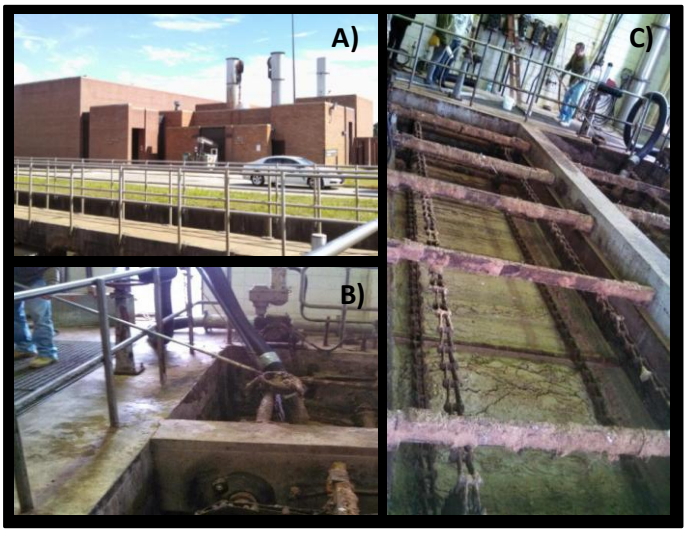


Figure 2.3: Sewage scum grease waste sampling: (A) primary tank next to sewage scum concentration building; (B) sampling of sewage scum grease from scum concentration tank; (C) aerial view of scum concentration tank.

SSG samples were drained prior to the GLE procedure in which they were fractionated into lipids, solids, and extraction wastewater. The water effluent of the primary tank and SCB (underflow water-UW), the drained water during the GLE (filtered water-FW), and the extraction water (EW) were all sampled throughout the process to test the water quality. Water sampling points are indicated with a star (*) in Figure 2.1.

2.2.3. Grease Lipid Extraction (GLE)

The wastewater grease fractionation step was performed both at PWD and Drexel using a standard operating procedure which is referred to as grease lipid extraction (GLE); the GLE method was modified slightly based on equipment available at each site. GLE was performed on the floating layer of the GTW and of the partially dewatered

SSG. The GLE method was developed from preliminary experiments to optimize lipid separation from wastewater greases (Appendix A.1.1). We have observed that GTW lipids separated by heating and settling more easily than SSG lipids; however, to enhance lipid separation, the GLE method included lowering the pH of the raw grease samples using sulfuric acid prior to heating and settling. A flow diagram of the GLE process is shown in Figure 2.4.

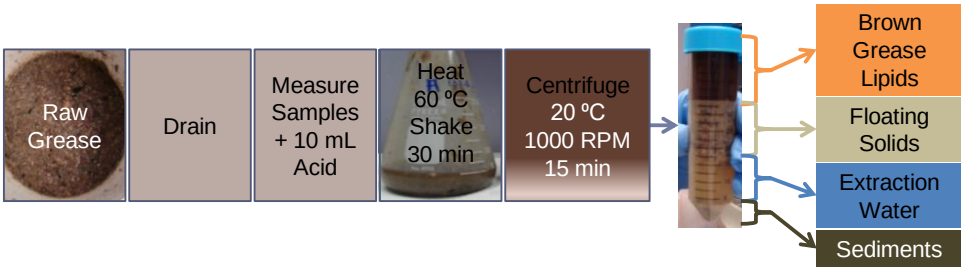


Figure 2.4: Grease lipid extraction (GLE) procedure.

Samples of wet raw grease were mixed by hand to homogenize the mixture. For samples of SSG, some large trash objects such as twigs, plastic wrappers, and paper were removed when taking a sample for GLE. Approximately 200 g of wet raw grease was strained for 15 min to remove excess free water. Four replicate GLE experiments were processed at a time for each sample of raw waste grease. For each replicate, about 40 g of strained raw grease was placed into a 250 ml glass Erlenmeyer flask. 10 ml of 10% sulfuric acid in water solution was added to each Erlenmeyer flask. Each flask was lightly capped; the mixture was heated at 60 °C and shaken for 30 min. The mixture in each individual flask was transferred to an individual 50 ml centrifuge tube and centrifuged at about 1,000 RPM for 15 min. After centrifuging, four layers within the

centrifuge tube were observed from top to bottom: (1) brown grease lipids, (2) floating solids, (3) extraction wastewater, and 4) sediments. The mass and volume of each of these layers were measured. The mass of each layer was divided by the starting mass to give a percent mass of each layer shown in Equation 2.1:

$$\%m_i = \frac{m_{i,fractionated}}{m_{\,starting\ raw\ grease}} \times 100 \qquad \text{(Eq. 2.1)}$$

Where,

m = mass

i = layer; brown grease lipids, floating solids, extraction wastewater, or sediments

Because of the addition of the sulfuric acid, the sum of the mass of each layer is above 100%.

At PWD, the GLE procedure was scaled up to 500 ml volumes of SSG to produce enough secondary wastewater for water quality testing. The following is a list of differences between analytical methods at PWD and Drexel University:

- PWD experiments used larger scum samples (~500 ml) compared to Drexel (~40 ml).
- The centrifuge used at PWD was able to produce higher centripetal accelerations.
- The Drexel extractions used a higher degree of agitation during the heating and shaking stage.
- PWD extractions were performed within 24 hours after sample collection. Drexel extractions were performed days, weeks, or months later, but samples were stored in a cold room (~7°C) until the extraction experiments were performed.
- In samples containing a significant amount of trash, it was often difficult to obtain consistent experimental samples – which lead to higher variability both in the initial experimental sample at PWD and in later experiments performed at Drexel.

A comparison of the results from the Drexel and PWD extractions is shown in Appendix A.1.2. Figure A.3 shows there was a strong correlation between the GLE lipid extraction performed at Drexel and PWD (significant below 0.01 level). There was no correlation (not significant below 0.05 level) between the total acid number (measurement of lipid quality discussed in the next section) of Drexel extracted samples and PWD extracted samples. Drexel samples for GLE were stored longer prior to GLE which could be a cause for the lack of correlation.

2.2.4. Brown Grease Lipid Quality

The free fatty acid (FFA) content of the lipids was measured using titration. Potassium hydroxide was dissolved in a 20% volume water in methanol solution to make a 0.1 M titrant. A solvent of 50% volume toluene in isopropanol with phenolphthalein indicator was used to dissolve approximately 0.3-0.5 g of brown grease lipids.

The total acid number (TAN) of the lipids was calculated to determine the amount of KOH needed to reach the slightly pink endpoint per gram of sample titrated. This calculation was determined using Equation 2.2:

$$TAN = \frac{V_{Titrant} M_{Titrant} MW_{KOH}}{m_{Sample}} = \frac{mg_{KOH}}{g_{Sample}} \qquad \text{(Eq. 2.2)}$$

Where,

$V_{Titrant}$ = *volume of titrant, ml*

$M_{Titrant}$ = *molarity of titrant, mol/L*

MW_{KOH} = *molecular weight of potassium hydroxide, g/mol*

m_{Sample} = *mass of sample titrated, g*

The TAN number was normalized to a percentage FFA value on an oleic acid basis by dividing by 198.6 mg KOH/g Sample, which is the TAN of pure oleic acid.

While using the %FFA on an oleic acid basis is not as accurate as gas chromatography techniques, it provided an approximate value for %FFA and was simple and quick to perform on a large number of samples.

2.2.5. Wastewater Quality

For wastewater samples from GTW, the water quality was characterized by chemical oxygen demand (COD) and total solids. The COD was tested according to Hach Company method 8000 for water, wastewater and seawater (Hach, 2010). Total solids in the wastewater was determined according to Hach Company method 8271 for potable, surface and saline water and for domestic and industrial wastewater (Hach, 2012).

PWD performed additional wastewater quality testing on the underflow water, filtered water, and extraction water. They provided testing of COD, total Kjeldahl nitrogen (TKN), total solids, volatile solids, ammonia, pH, conductivity, and alkalinity.

2.2.6. Statistical Analysis

Statistical analysis was performed using IBM SPSS Statistics 23 (IBM, 2015). The Pearson coefficient indicated the trend of the correlation (positive or negative) and the significance indicated the strength of the correlation. Significance values above 0.05 are not considered significant; values below 0.05 and above 0.01 are considered weakly significant; values below 0.01 are considered significant.

The parameters studied for correlations of GTW and SSG are shown in Table 2.1. The boxes are colored to identify similar parameter groupings. External factors such as temperature, precipitation, and time of year are grouped as green. Extracted lipids and TAN are grouped in orange; extracted solids are grouped in brown; and extracted water is

grouped in blue. The water quality parameters for the tank water (GTW) and underwater (SSG) are grouped in purple. The water quality parameters for the extraction water are grouped in light red.

Table 2.1: Grease trap waste and sewage scum grease parameters studied for correlation analysis.

Grease Trap Waste
Sampling month
Into the tank month
Days in tank
Daily average temperature (°C)
Volume of extractable lipids in tank (%)
Separated GTW float grease layer in tank (%)
Separated wastewater layer in tank (%)
Separated sediments layer in tank (%)
Volume of extractable lipids in GTW float grease layer (%)
TAN/%FFA of lipids (mgKOH/g)
Tank wastewater total solids (%)
Tank wastewater COD (mg/L)

Sewage Scum Grease
Source of SSG: PWD WRRF plant (NE, SE, SW)
Source of SSG: PWD WRRF location (PTE, SCB)
Source of SSG: PWD WRRF plant and location
Sampling 16 month (1-16): total range of composition data
Sampling 12 month (1-12): official longitudinal study range
Average temperature (°C)
5-day average precipitation (mm)
%Lipids of SSG sample
%Water of SSG sample
%Wet solids of SSG sample
Tan/%FFA of lipids (mgKOH/g)
Underflow water COD (mg/L)
Underflow water total Kjeldahl Nitrogen (mg/L)
Underflow water total solids (%)
Underflow water volatile solids (%)
Underflow water ammonia (mg/L)
Underflow water pH
Underflow water conductivity (uS/cm)
Underflow water alkalinity (mg/L)
Extraction water COD (mg/L)
Extraction water total Kjeldahl Nitrogen (mg/L)
Extraction water total solids (%)
Extraction water volatile solids (%)
Extraction water ammonia (mg/L)
Extraction water pH
Extraction water conductivity (uS/cm)
Extraction water alkalinity (mg/L)

2.3. Results and Discussion

2.3.1. Longitudinal Study Grease Trap Waste Results

2.3.1.1. Grease Trap Waste Composition

GTW was sampled 35 times from the RRWM settling tank. The total volume of raw GTW in the collection tank ranged between 1110-1728 L (293-457 gal) with an average of 1431 L (379 gal). GLE was performed only on the top floating grease layer.

Figure 2.5 displays the volume of each of the layers in the tank; however, the floating grease layer was represented as two components based on GLE results: (1) the extractable brown grease lipids (orange) and (2) wet floating solids which are the remainder of the floating grease (tan).

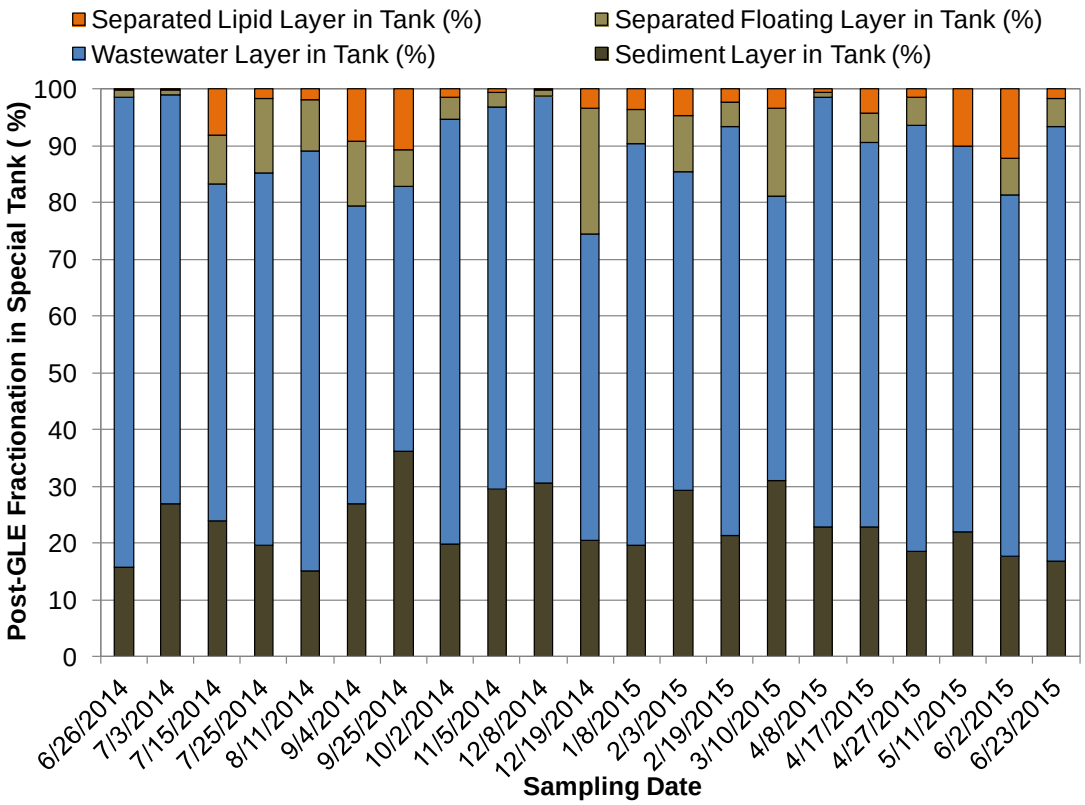


Figure 2.5: Separation of grease trap waste into layers by settling at ambient temperature. The floating grease layer is shown as two layers: (1) the amount of extractable lipids (orange) and (2) the rest of the floating wet solids (tan). Remaining layers are wastewater (blue) and sediments (brown).

The brown grease lipid layer volume varied between 0.2-12.1% of the raw GTW volume with an average of 3.9%. However, the brown grease lipid content can also be expressed as a volume of the float layer to represent concentration of the brown grease

from gravity settling alone. Brown grease content of the float grease layer varied between 11-100% with an average of 34% which showed a 750% increase in brown grease content. The wet solids in the floating layer ranged between 0-22% of the raw GTW volume with an average of 7%. The wastewater layer (blue) was 47-83% of the raw GTW volume with an average of 66%. The wastewater layer had the largest volume of material and the highest variability of the layers observed during sampling. The sediment layer (brown) in the tank varied between 15-35% of the raw GTW volume with an average of 23%.

2.3.1.2. Grease Trap Waste Tank Water Quality

The water quality of the GTW tank water is shown as a box plot in Figure 2.6. The box portion represents the 25-75 percentiles, the whiskers represent the 5-95 percentiles, the filled square represents the mean, and the straight horizontal line represents the median.

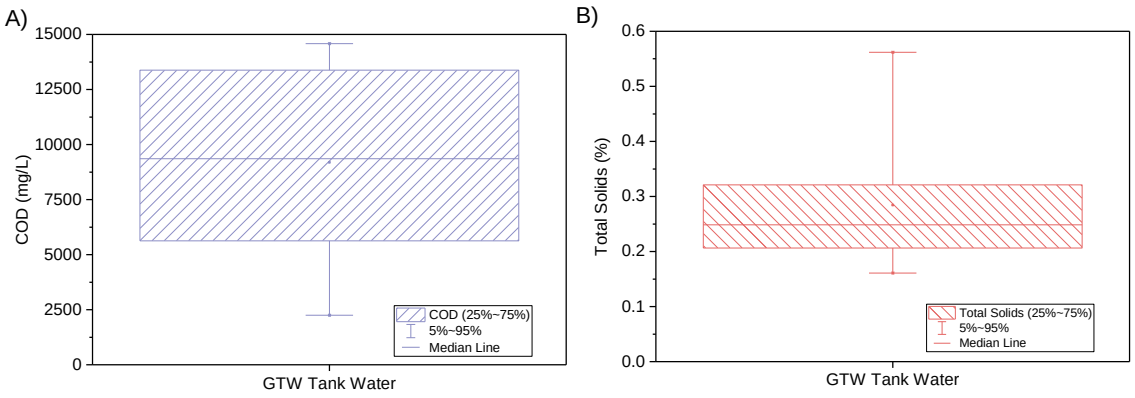


Figure 2.6: Quality of wastewater sampled from grease trap waste sampling tank for (A) chemical oxygen demand (COD) and (B) total solids.

The average COD was 9,192 mg/L with a standard deviation of 4,665 mg/L. The COD of the tank water varied greatly with a minimum of 2,247 mg/L and a maximum of 1,4580 mg/L. The average total solids content in the tank water was 0.28% with a standard deviation of 0.13%. The total solids content in the GTW tank water was generally between 0.20-0.32% except for one sample at each extreme with a minimum of 0.16% and maximum of 0.56%.

2.3.1.3. Grease Trap Waste Correlations

Correlations were sought between pairs of all data sets (Table 2.2). The table shows the correlated parameters, Pearson correlation, significance (Sig.), number of samples (N), and the relevance of the correlation. The table shows the correlated parameters, Pearson correlation, significance (Sig.), number of samples (N), and the relevance of the correlation. The table is divided between significant correlations (** correlation is significant at the 0.01 level) and weakly significant (* correlation is significant at the 0.05 level).

The first three rows of Table 2.2 are the strongest identified correlations that are between the depth of the wastewater layer and the depths of the sediment layer, the float grease layer and the extractable lipids. These pairs of correlated parameters are related to mass balances; for example, if the percent water that separates increases, it is necessary that either the lipid content or wet solids will decrease. When the water content of GTW is higher and the wastewater layer is thicker, this correlates to less sediments, less float grease, and less lipids. These correlations between the thickness of the wastewater layer (i.e. the dilution of the GTW) and the solid layers are not surprising. Plots of these correlations are shown in Appendix A.2.1.

Table 2.2: Summary of the significant correlations found in grease trap waste.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Separated Wastewater Layer in Tank (%)	**Separated Sediment Layer in Tank (%)**	-0.679**	3.53E-04	21	Depth of Water Layer inversely related to depth of sediments	SIGNIFICANT
Separated Wastewater Layer in Tank (%)	**Separated GTW Float Grease Layer in Tank (%)**	-0.650**	7.11E-04	21	Depth of Water Layer inversely related to depth of float grease	
Separated Wastewater Layer in Tank (%)	**Volume of Extractable Lipids in Tank (%)**	-0.609**	1.70E-03	21	Depth of water layer inversely related to extractable lipids	
Separated GTW Float Grease Layer in Tank (%)	**COD of Wastewater (mg/L)**	0.910**	2.21E-03	7	Higher COD correlates with more float grease	
Total Solids of Wastewater (mg/L)	**Sampling Month**	-0.897**	3.14E-03	7	Total solids decreases during warmer months	
Total Solids of Wastewater (mg/L)	**Average Temperature (ºC)**	-0.819*	1.21E-02	7	Total solids decreases during warmer months	WEAKLY SIGNIFICANT
Volume of Extractable Lipids in GTW Float Grease (%)	**Total Acid Number (%FFA) of Lipids (mg KOH/g)**	-0.446*	4.76E-02	15	Acid number weakly inversely related to the amount of extractable lipids	

** Correlation is significant at 0.01 level. * Correlation is significant at 0.05 level.

2.3.2. Longitudinal Study Sewage Scum Grease Results

2.3.2.1. Sewage Scum Grease Composition

SSG was sampled 61 times from SCBs at PWD during the longitudinal study and each sample was fractionated using the GLE procedure. The results presented in this thesis are monthly averages of the SSG samples; data from individual samples were summarized for a Water Environment Research Foundation (WERF) report (Cairncross et al., 2015). Figure 2.7 displays the monthly averages of the amounts of the GLE fractions of SSG; the total percentage of the factions is above 100% because the percent mass was calculated based on the starting wet grease mass and sulfuric acid solution that was added during GLE.

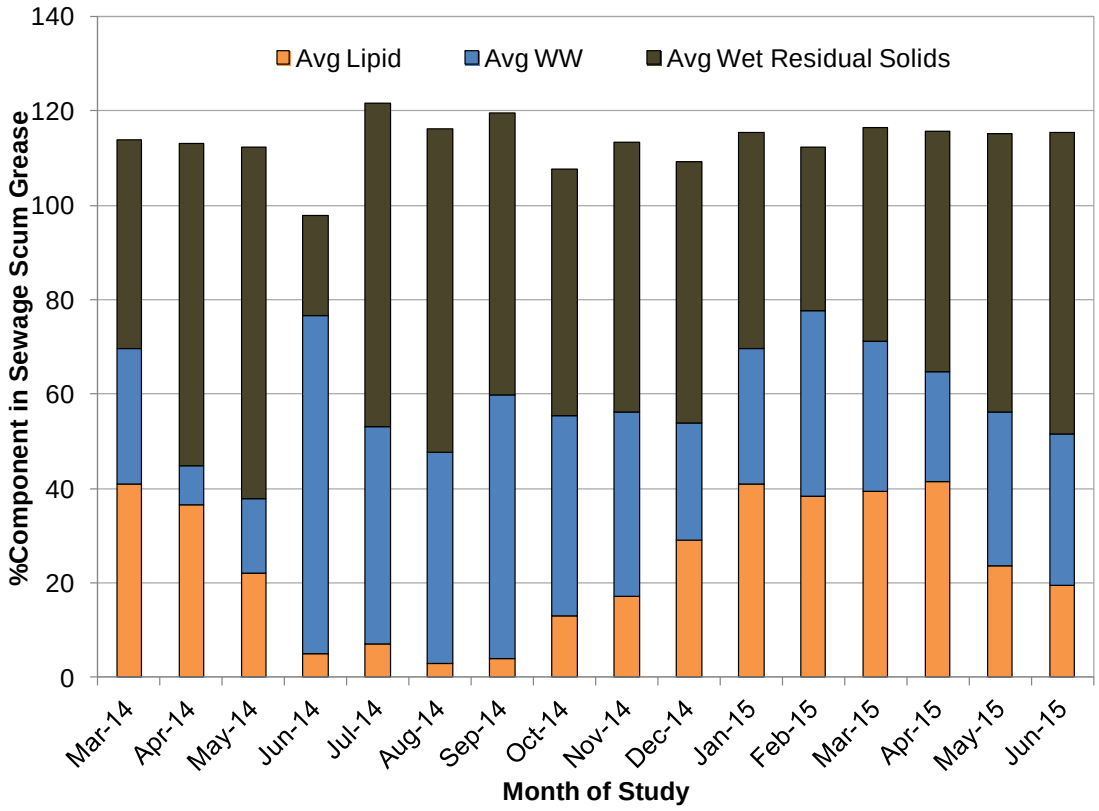


Figure 2.7: Fractions of sewage scum grease averaged by month of the study.

The monthly average secondary wastewater fraction had the largest range between 8-72% of initial sample volume followed by the wet residual solids (including both floating solids and sediments) with 21-74%. The largest values of monthly average lipid content were in March 2014, January 2015, and April 2015 with over 40% lipids while the lowest monthly average lipid content was recorded in August 2014 with only 3% lipids.

2.3.2.2. Sewage Scum Grease Water Quality

Individual water quality sampling was performed (not monthly averages) of the tank water and is shown as box plots in Figure 2.8. The box portion represents the 25-75 percentiles, the whiskers represent the 5-95 percentiles, the filled square represents the

mean, the straight horizontal line represents the median, and the star represents the minimum and maximum.

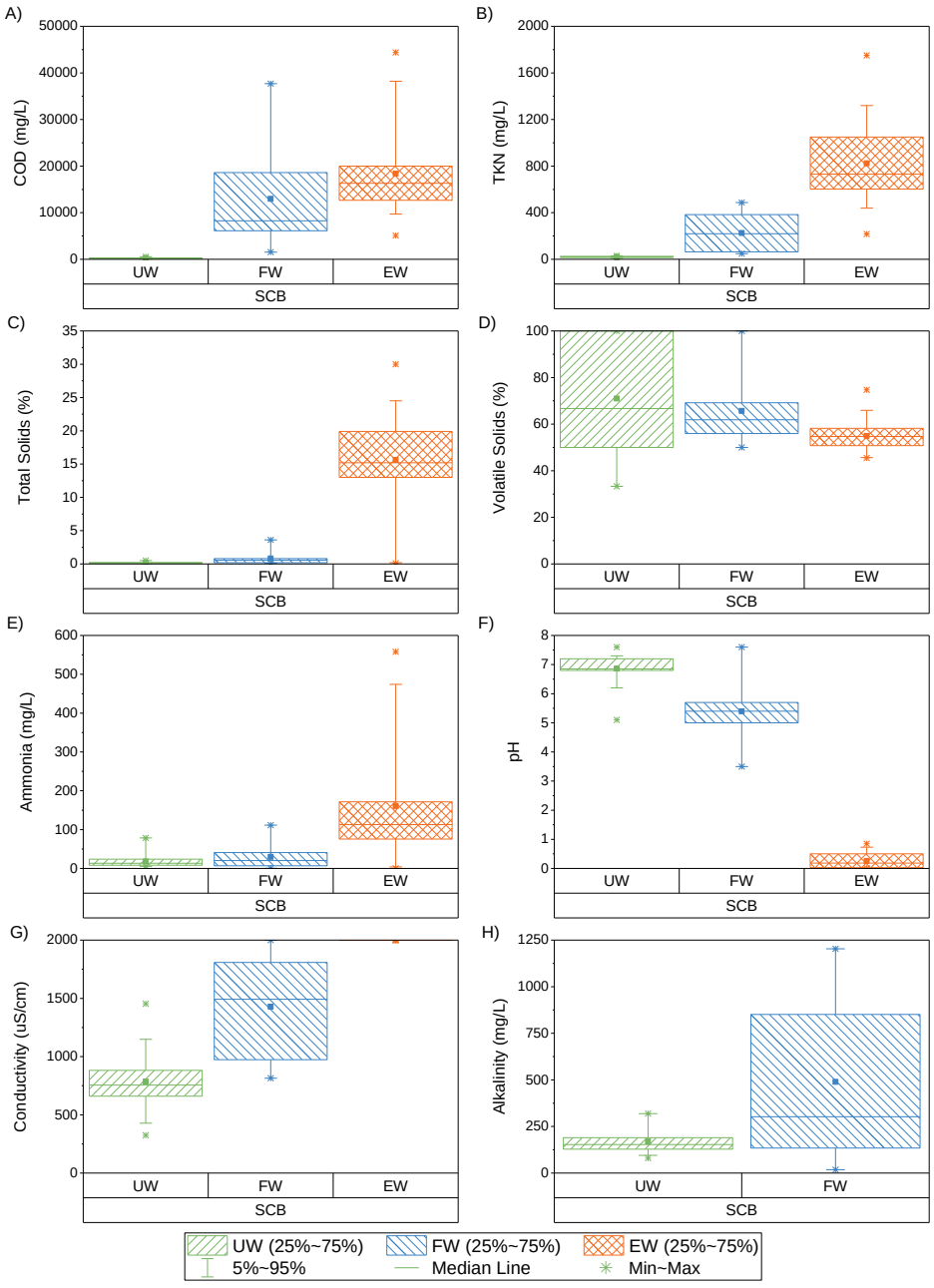


Figure 2.8: Scum concentration building water quality testing of underwater (UW), filtered water (FW), and extraction water (EW) for (A) chemical oxygen demand (COD), (B) total Kjeldahl nitrogen (TKN), (C) total solids, (D) volatile solids, (E) ammonia, (F) pH, (G) conductivity, and (H) alkalinity.

For all water quality metrics but volatile solids and pH, the intensity of the metric became higher with each grease processing stage. The underflow water (UW) had a low value, as the raw SSG is filtered, the filter water (FW) had a higher value, and finally the extraction water (EW) had the highest value. This trend of increasing concentration of contaminants is related to the trend that at each processing step there was a smaller volume of water being separated from the solids. The volatile solids of the three water samples were similar with the highest range in the underwater samples. The trend for pH was UW>FW>EW because of the acid added during the GLE which lowers the pH. The conductivity of the extraction water samples was consistently greater than 1,999 uS/cm which was the detection limit of the test. The extraction water had high concentration of contaminants and a low pH; however the volume of extraction water that would be produced by the process is orders of magnitude smaller than the underwater volume processed at a WRRF.

2.3.2.3. Sewage Scum Grease Correlations

Correlations were sought between pairs of all data sets (Table 2.1) collected for SSG. Table 2.3 shows significant correlations (** correlation is significant at the 0.01 level) and Table 2.4 shows significant (* correlation is significant at the 0.05 level). The tables show the correlated parameters, Pearson correlation, significance (Sig.), number of samples (N), and the relevance of the correlation. The parameters that appear most frequently in the significant correlations are “% Lipids of SSG Sample” (8 times), “Extraction WW – COD” (7 times), “Sampling Month” (4 times), “Daily AVG temp” (3 times), and other extraction wastewater parameters (2-4 times each).

Table 2.3: Summary of the significant correlations found in sewage scum grease.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Extraction Water - Nitrogen (TKN)	Extraction Water - Ammonia (mg/L)	.747**	1.96E-11	56	WW correl	SIGNIFICANT CORRELATION
% Water of SSG Sample	% Lipids of SSG Sample	-.659**	5.25E-09	60	mass balance	
% Lipids of SSG Sample	Daily AVG Temp (ºC)	-.650**	9.71E-09	60	seasonal variation	
% Lipids of SSG Sample	Sampling 12 Month (1-12)	-.616**	7.98E-08	60	seasonal variation	
Extraction Water - Total Solids (%)	% Lipids of SSG Sample	.540**	5.09E-06	59	higher lipids leads to more contaminants in WW	
% Wet Solids of SSG Sample	Daily AVG Temp (ºC)	.502**	2.22E-05	60	seasonal variation	
Extraction Water - COD (mg/L)	Extraction Water - Total Solids (%)	.485**	8.65E-05	55	WW correl	
Extraction Water - Nitrogen (TKN)	Extraction Water - COD (mg/L)	.480**	1.04E-04	55	WW correl	
Extraction Water - Total Solids (%)	% Water of SSG Sample	-.449**	1.78E-04	59	higher lipids leads to more contaminants in WW	
Daily AVG Temp (ºC)	Sampling 12 Month (1-12)	.442**	2.05E-04	60	temp varies with season - not part of study	
Extraction Water - COD (mg/L)	% Lipids of SSG Sample	.440**	3.83E-04	55	higher lipids leads to more contaminants in WW	
Extraction Water - COD (mg/L)	% Water of SSG Sample	-.418**	7.44E-04	55	higher lipids leads to more contaminants in WW	
% Wet Solids of SSG Sample	% Lipids of SSG Sample	-.373**	1.68E-03	60	mass balance	
Extraction Water - COD (mg/L)	Sampling 12 Month (1-12)	-.379**	2.19E-03	55	seasonal variation	
Underflow Water - Volatile Solids (%)	Extraction Water - Ammonia (mg/L)	.616**	2.50E-03	19	WW correl	
Underflow Water - Nitrogen (TKN)	Extraction Water - COD (mg/L)	-.626**	2.70E-03	18	WW correl	
Underflow Water - Nitrogen (TKN)	Underflow Water - Volatile Solids (%)	-.688**	3.29E-03	14	WW correl	
Underflow Water - Volatile Solids (%)	Extraction Water - Nitrogen (TKN)	.590**	3.92E-03	19	WW correl	
Extraction Water - Ammonia (mg/L)	% Lipids of SSG Sample	-.345**	4.58E-03	56	higher lipids leads to less nitrogen in WW	

** Correlation is significant at 0.01 level.

Table 2.4: Summary of the weakly significant correlations found in grease trap waste.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Underflow Water - COD (mg/L)	Extraction Water - Total Solids (%)	-.472*	1.54E-02	21	WW correl	WEAKLY SIGNIFICANT CORRELATION
% Water of SSG Sample	Sampling 12 Month (1-12)	.257*	2.37E-02	60	seasonal variation	
Underflow Water- Alkalinity (mg/L)	Sampling 12 Month (1-12)	.406*	2.44E-02	24	seasonal variation	
% Water of SSG Sample	Daily AVG Temp (ºC)	.251*	2.66E-02	60	seasonal variation	
Underflow Water - Ammonia (mg/L)	Underflow Water - Volatile Solids (%)	-.506*	2.72E-02	15	WW correl	
Extraction Water - COD (mg/L)	Daily AVG Temp (ºC)	-.261*	2.73E-02	55	seasonal variation	
Underflow Water - Conductivity (uS/cm)	Daily AVG Temp (ºC)	-.416*	3.05E-02	21	seasonal variation	
Extraction Water - Volatile Solids (%)	Extraction Water - Total Solids (%)	.239*	3.39E-02	59	WW correl	
Underflow Water - pH	Underflow Water - Nitrogen (TKN)	-.452*	3.44E-02	17	WW correl	
Underflow Water - Conductivity (uS/cm)	Underflow Water - Volatile Solids (%)	-.445*	3.66E-02	17	WW correl	
Underflow Water- Alkalinity (mg/L)	Daily AVG 5-day AvgPrecip (mm)	-.371*	3.70E-02	24	seasonal variation	
Extraction Water - Ammonia (mg/L)	Daily AVG 5-day AvgPrecip (mm)	.241*	3.71E-02	56	seasonal variation	
Extraction Water - Ammonia (mg/L)	Sampling 12 Month (1-12)	.239*	3.80E-02	56	seasonal variation	
Extraction Water - Nitrogen (TKN)	Extraction Water - Volatile Solids (%)	.235*	3.81E-02	58	WW correl	
Underflow Water - COD (mg/L)	Extraction Water - Nitrogen (TKN)	.395*	3.81E-02	21	WW correl	
Extraction Water - Total Solids (%)	Daily AVG Temp (ºC)	-.230*	3.98E-02	59	seasonal variation	
Underflow Water - pH	Underflow Water - Volatile Solids (%)	.420*	4.12E-02	18	WW correl	
Underflow Water - Ammonia (mg/L)	Extraction Water - Ammonia (mg/L)	.407*	4.17E-02	19	WW correl	
Underflow Water - Volatile Solids (%)	Daily AVG 5-day AvgPrecip (mm)	.399*	4.52E-02	19	seasonal variation	
Extraction Water - Nitrogen (TKN)	Daily AVG Temp (ºC)	.224*	4.55E-02	58	seasonal variation	

* Correlation is significant at 0.05 level.

Several of the most significant correlations related to seasonal variations in the composition of SSG and the corresponding wastewater streams. Seasonal variation was shown by correlations between (in order of highest to lowest significance) percent lipids of SSG (Figure 2.9), percent wet solids of SSG, extraction wastewater COD, extraction

wastewater total solids, percent water of SSG sample, underwater conductivity, extraction water ammonia, extraction water total solids, and extraction water nitrogen and either the daily average temperature or the sampling month.

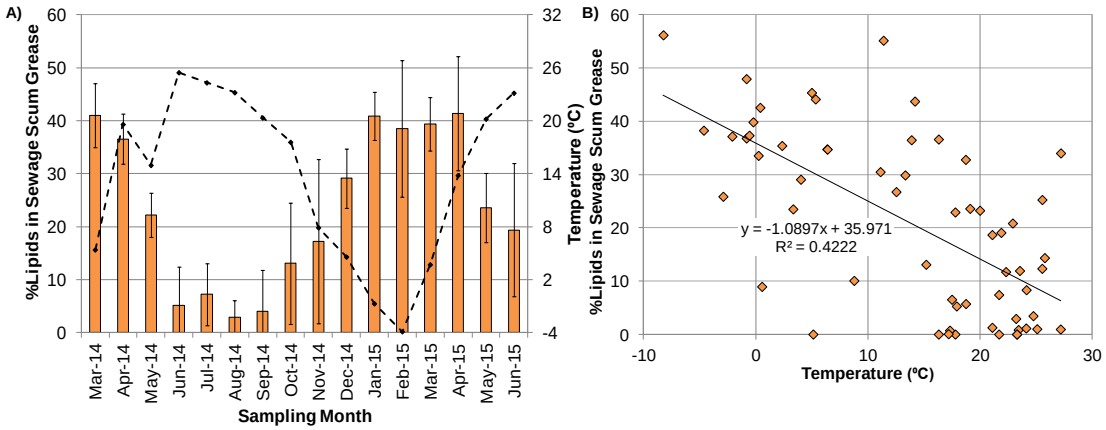


Figure 2.9: Temperature effect on lipid content: (A) monthly lipid content and temperature and (B) lipid content versus temperature.

The monthly lipid content was compared to ambient temperature at sampling (Figure 2.9-A) showing opposite sinusoidal trends between lipid content and temperature. As temperature decreased, the brown grease lipid content increased. This dependence on temperature is further shown by plotting lipid content versus temperature (Figure 2.9-B). A line was fit to the data series and the R-squared value is low due to the variability of lipid content; however, the overall inverse correlation between lipid content and temperature is still visible. There were also visual differences between the SSG samples with low and high lipid contents as shown in Figure 2.10.

Figure 2.10: Photos of sewage scum grease samples obtained from various locations and at different times of the year.

Figure 2.10-A displays a sample of SSG collected in the cooler season with a large amount of extractable lipids. The grease was brown and granular with small amounts of trash. Figure 2.10-B displays a sample of SSG collected in the warmer season, but contained a large amount of trash which made lipid extraction difficult. Figure 2.10-C shows a sample of SSG collected in the warmer season that did not produce lipids; this SSG was a thick, black material that was visually similar to sewage sludge.

The extraction water COD had highly significant correlation with four other water quality metrics of the extraction water, with the percent lipids in SSG, and with season. In addition, many of the significant correlations were between wastewater parameters – either different wastewater quality metrics in the same stream or between the underwater stream and the extraction water. Most of these wastewater correlations ("WW correl" in Table 2.3) were positive correlations, for example TKN, total solids and volatile solids were all positively correlated with COD in the extraction water (Figure 2.11).

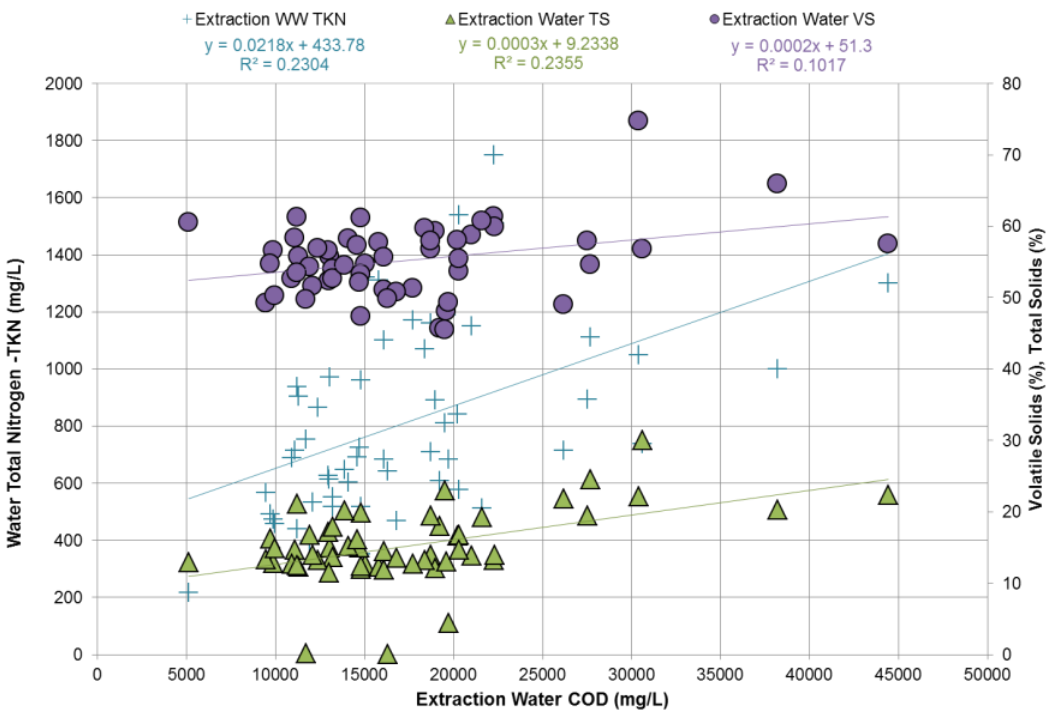


Figure 2.11: Correlations between extraction water quality metrics.

The high TKN, high ammonia, and high COD content of the extraction water may imply a high level of biodegradable organic carbons, which would suggest a high BOD. However, during the extraction procedure, acid was added to SSG which lowered the pH to less than 1.0, which would eliminate biological activity; therefore, BOD of the extraction water samples was not studied in this project.

During the longitudinal study, variability in the lipid content of SSG obtained from the three different PWD water pollution control plants was observed (Figure 2.12).

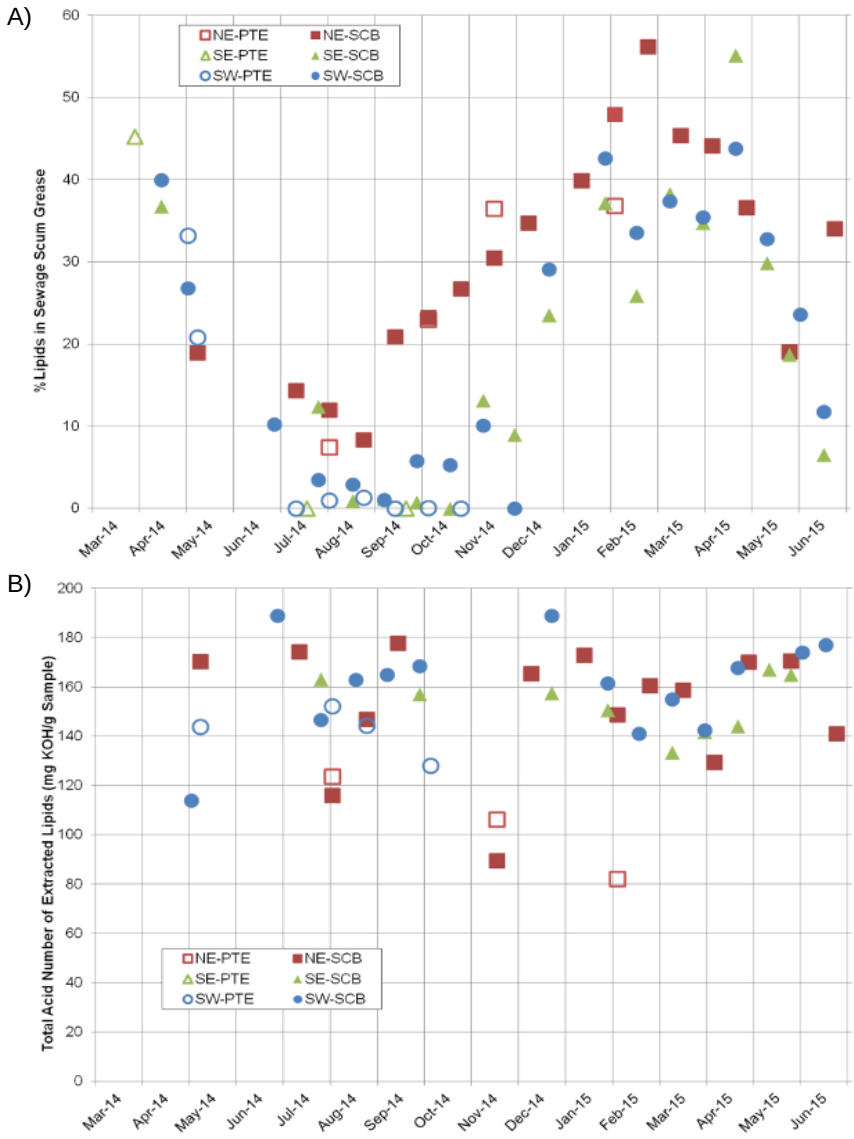


Figure 2.12: Comparison of (A) lipid content and (B) total acid number of sewage scum grease samples collected from at primary settling tank (PTE) and scum concentration building (SCB) at three wastewater recovery resource facilities: (1) Northeast (NE), (2) Southeast (SE), and (3) Southwest (SW).

The lipid content at the Northeast (NE) facility appeared generally higher than SSG from the other plants; however, this difference was not statistically significant. One-way ANOVA was performed in SPSS using Tukey's method to determine the lipid content difference of averages between each of the sampling locations. The only

significant difference found was between the lipid contents of Southwest (SW) primary tank and NE SCB; however there were only three SW primary tank samples for comparison. Otherwise, there was not a statistically significant difference between the extractable lipids from SSG samples obtained from all of the locations.

2.3.3. Grease Trap Waste and Sewage Scum Grease Lipid Content Comparison

Histograms of GTW and SSG lipid and FFA contents were compared in Figure 2.13. Because there were more samples of SSG than GTW, the y-axis displays a normalized frequency by dividing the number of occurrences in that specified range by the total number of samples in the data category. Figure 2.13-A shows the lipid content comparison between the raw GTW (brown grease, floating solids, wastewater, and sediments) and just the floating solids layer. The majority of lipid contents for raw GTW were below 10% while the floating layer content had more variability. The average lipid content for the raw GTW and floating layer was 4% and 32%, respectively. Figure 2.13-B shows there was very little difference between the FFA content of GTW and SSG brown grease lipids. There were more low-FFA brown grease lipids for SSG than GTW but majority of samples ranged from 70-90 %FFA. The average FFA content for GTW and SSG was 77% and 76%, respectively. Figure 2.13-C shows the seasonal variability of the SSG lipid content. There is overlap between the most of the samples in the warm and temperate seasons; however, the warm season had the largest number of samples in the 0-10% lipid content range. The 20-30% lipid contents were the only range that had samples from each season. The average lipid content for the warm, temperate, and cool season was 7%, 22%, and 40%, respectively. Figure 2.13-D showed that FFA was not seasonally dependent. All SSG FFA contents overlapped with the majority of samples in

the 60-80% range. The average FFA content for the warm, temperate, and cool season was 77%, 78%, and 75%, respectively.

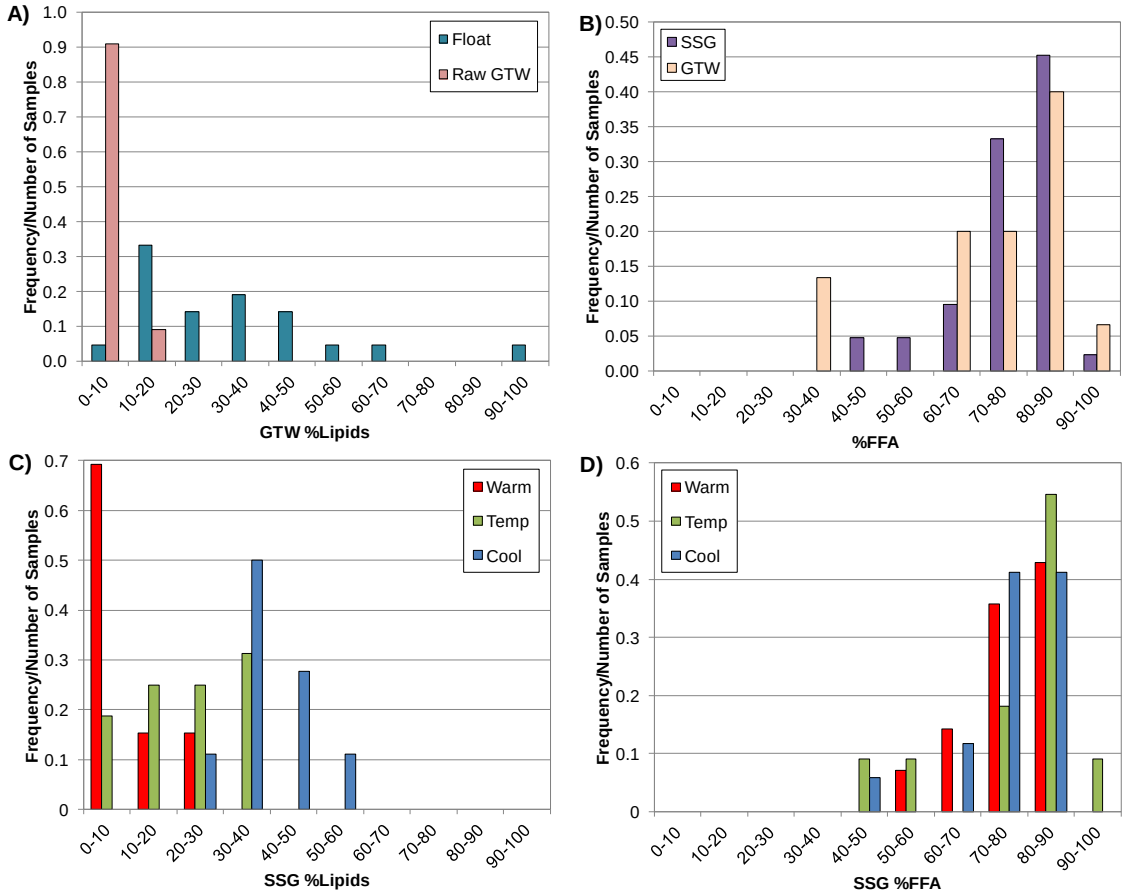


Figure 2.13: Histograms of grease trap waste (GTW) and sewage scum grease (SSG) lipid and free fatty acid (FFA) contents normalized by number of samples. Comparisons shown are (A) lipid content in the raw GTW and lipid content in the floating layer; (B) FFA content of GTW and SSG; (C) SSG lipid content by season; and (D) SSG FFA content by season.

2.4. Conclusions

Despite the large variability of the lipid content of each wastewater stream, there is a substantial amount of brown grease in GTW and SSG that can be extracted for biodiesel conversion. The overall lipid content in a tank of GTW was small (3%) but due

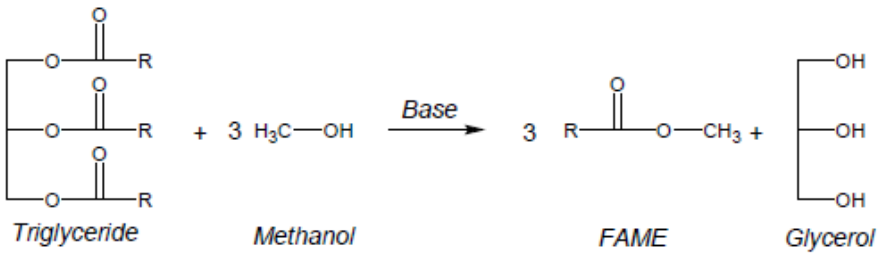
to the large amounts of GTW in the region, there is still a large volume of brown grease that is unutilized. Unexpectedly, SSG brown grease content had a significant correlation to collection temperature showing seasonal variability. This produces challenges if biodiesel production were to be implemented at a WRRF. However, both the grease hauler and WRRFs could implement a brown grease production plant and sell the brown grease to biodiesel producers.

The results presented in this chapter were also in partial fulfillment to a research grant provided by the Water Environment Research Foundation (WERF). In addition to this thesis, these results are also presented and WERF report (Cairncross et al., 2015) and research journal (Hums, Amin, et al., 2016) both of which will be subject to peer-review before publishing.

Chapter 3. Evaluation of Processing Biodiesel from Wastewater Greases

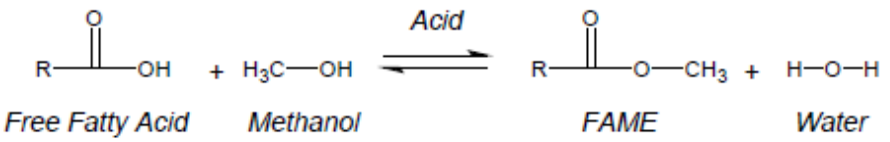
3.1. Introduction

The grease trap waste lipids (also known as brown grease) contain high levels of free fatty acids (FFA) which inhibits biodiesel production via conventional transesterification of refined vegetable oils. Vegetable oils contain high amounts of acyl-glycerides (primarily tri-acyl-glycerides, TAG) with low levels of FFA. The TAG can be converted through transesterification with an alcohol (in most cases methanol) and base catalyst to produce biodiesel as a fatty acid methyl ester (FAME) and by-product glycerol as shown in Scheme 3.1.



(3.1)

Brown grease lipids generally contain high amounts of free fatty acids due to the degradation of triglycerides. Transesterification is not viable for FFA content above 2% because of the formation of soaps (Canakci & Van Gerpen, 2001; Marchetti & Errazu, 2008; Ragauskas et al., 2013; Stacy et al., 2014). Instead, esterification is performed with an alcohol (typically methanol) and acid catalyst to produce water and FAME as shown in Scheme 3.2.



(3.2)

Materials containing a mixture of TAG and FFA typically undergo a two-step reaction by first performing esterification to convert FFA to FAME and followed by a transesterification to convert the remaining TAG to FAME. Alternative methods to the 2-step alkali catalyst include various types of reactions which includes super critical conditions (Lee et al., 2012; Vieitez et al., 2012; Yin et al., 2008), a variety of solid catalysts (Alsalme et al., 2008; Cao et al., 2008; Kiss et al., 2006), or enzymatic reactions (Guldhe et al., 2015; Nelson et al., 1996; Ranganathan et al., 2008).

Prior research at Drexel University has shown the feasibility of producing biodiesel from FFA (oleic acid) using a bubble column reactor (Stacy et al., 2014). The bubble column is effective at converting high-FFA lipid sources into FAME and the esterification of lipid at any FFA/TAG ratio (Stacy et al., 2014). The column is also robust at converting the FFA with a mixture of 80% methanol and 20% water which is beneficial when using recycled methanol (Stacy et al., 2014).

Previous studies involving brown grease to biodiesel production has shown difficulty in meeting the ASTM D6751 specification for sulfur content (Chakrabarti et al., 2008; Gardner et al., 2013; Kim et al., 2011). Brown grease lipids have shown sulfur content ranges between 188-400 ppm S and crude biodiesel between 160-390 ppm S (Chakrabarti et al., 2008; Gardner et al., 2013). Vacuum distillation has proven to be effective at reducing the sulfur content of biodiesel to 19-40 ppm S with 60-80% yield of distillate biodiesel (Chakrabarti et al., 2008). Post treatment with activated carbon can reduce sulfur content to 12 ppm S (Chakrabarti et al., 2008). Gardner et al. analyzed adsorption desulfurization and oxidant desulfurization techniques on crude biodiesel. The adsorption desulfurization batch methods included mixing various concentrations of

silica gel, polymers, activated carbon, and calcium oxide, and Zeolite; these methods removed 30-55% of sulfur (Gardner et al., 2013). The batch methods were not as effective as using a fixed column packed with mixtures of silica gel and alumina or activated carbon. The column adsorption methods were able to remove 19-75% of sulfur but still did not meet ASTM specification (Gardner et al., 2013). The oxidant desulfurization used hydrogen peroxide, acetic acid, or phosphotungstic acid to convert the non-polar sulfur species to polar sulfur species that could be removed through adsorption (Gardner et al., 2013). This combination of adsorption and oxidant desulfurization reduced sulfur content by up to 96% with some samples meeting ASTM specifications (Gardner et al., 2013). These techniques were able to reduce the sulfur content, but the product biodiesel yield and cost of additional materials are expensive which could impact the economic feasibility of a larger scale biodiesel production (Chakrabarti et al., 2008).

The goal of this chapter is to analyze the quality of biodiesel produced from GTW and SSG using a specialized reactor developed by Drexel University and EFR, LLC.

3.2. Biodiesel Production

This section will discuss the experimental methods used in producing biodiesel from brown grease extracted from GTW and SSG. A variety of operating conditions were explored experimentally in this project; however, this section presents the results using conditions from this project that were found to be effective in grease-to-biodiesel processing.

3.2.1. Esterification

The esterification reaction used in this work converts the free fatty acids (FFA) to fatty acid methyl esters (FAME), or crude biodiesel, using 1:9-1:12 brown grease to methanol molar ratio and 0.3-0.5% g sulfuric acid/g brown grease. The reaction was run at atmospheric pressure and approximately 120 °C for 3 hours. Running the reactor above the boiling point of water allowed for the co-product water to be removed from the reaction to increase biodiesel yield (Figure 3.1). The un-reacted methanol and water exited the reactor as a vapor which could be condensed and recycled (depending on the purity of the methanol) or could be distilled in a larger-scale operation for recycling. In some cases, the methanol condensate was collected and the density was analyzed using a hygrometer to determine the purity of the methanol. The total acid number (TAN) was measured (measured using the titration procedure described in Section 2.2.4) throughout the experiments to determine the amount of remaining FFA.

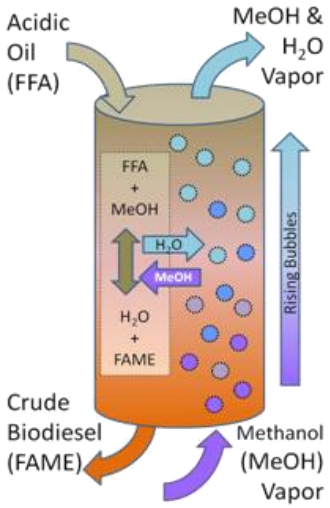


Figure 3.1: Schematic of esterification in bubble column reactor.

The reactor designs were based on initial experiments performed by Stacy et al. (Stacy et al., 2014) and a number of other bubble reactors constructed by Drexel student researchers. Biodiesel esterification was performed in a variety of reactors as shown in Figure 3.2-A with a summary of each reactor in Table 3.1.

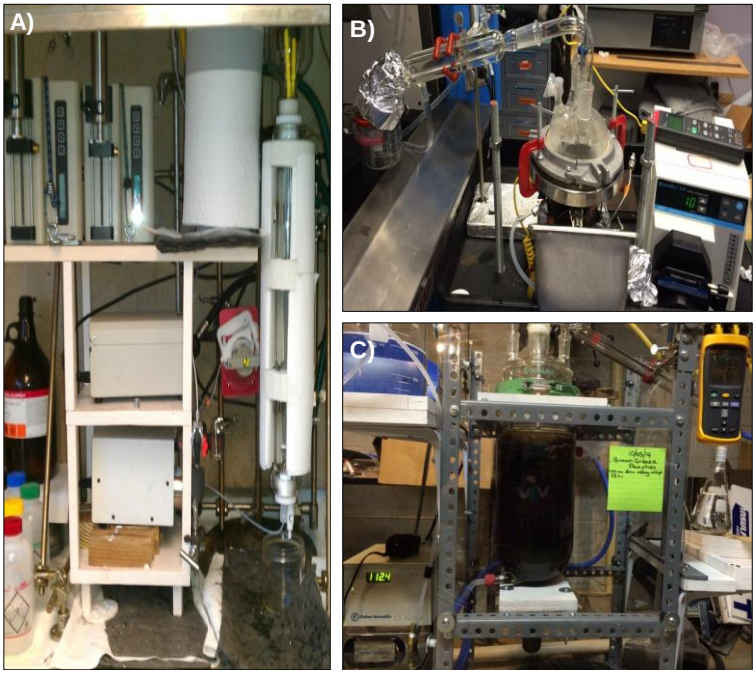


Figure 3.2: Biodiesel bubble column reactors used for esterification of brown grease lipids to biodiesel: (A) 250 ml glass; (B) 1.5 L stainless steel; and (C) 4 L glass.

Table 3.1: Comparison of bubble column reactors.

	Test Tube	Glass Column (Stacy)	Stainless Steel Column (Melick)	EFR, LLC
Volume	50 ml	250 ml	1.5 L	4 L
Material	Glass	Glass	Stainless Steel	Glass
Heating	Oil Bath	Jacketed Oil Circulation	Electric	Jacketed Oil Circulation
Vapor Condenser	No	No	Yes	Yes
Recirculation of Reaction	No	Yes	Yes	No
Methanol Pre-vaporizer	No	Yes	Yes	Yes
Agitation	No	No	No	Yes

Small experiments could be performed in a 50 ml test tube reactor (image not shown) to convert about 20 ml of FFA to FAME. The test tube was partially submerged in an oil bath and heated to 120 ºC. Methanol was added with a peristaltic pump and sulfuric acid catalyst was slowly added using a pipette. These reactions were difficult to control because if the addition of the acid or methanol was too fast, the reaction bubbled over the test tube and a significant amount of reactants were lost to the oil bath. This problem has not occurred with the larger reactors.

The first larger reactor was designed by Stacy et al. (Figure 3.2-A) was an 18 in tall, 1 in interior diameter, jacketed glass column with a total volume of about 250 ml that could convert about 180 ml of brown grease (Stacy et al., 2014). The reactor utilized syringe pumps for a methanol delivery (45 ml/min) that ran through a heat exchanger to deliver the methanol as a vapor to the reactor. The glass column was heated to 120 ºC with silicon oil and insulated. The sulfuric acid catalyst (0.5%wt to brown grease) in methanol was delivered using a peristaltic pump in the first five minutes of the reaction. The contents of the reactor were re-circulated from the bottom of the reactor, through the heat exchanger and delivered back through the top of the reactor. The reaction typically ran between 2-3 h. Sampling of the FAME throughout the reaction was done using a valve at the bottom of the reactor. About 20 ml of material would be drained prior to sampling to ensure that the sample was the best representation of the column and not residual material from the previous sample. The 20 ml of material was then poured back into the top of the reactor. Three drawbacks to this reactor were (1) it was not equipped to collect the methanol and water vapor exiting the reactor, (2) the brown grease lipids would solidify in the re-circulation line, and (3) the crude FAME volumes were small for

the amount of biodiesel needed for testing after downstream steps for washing, purification, and ASTM testing.

The 1.5 L stainless steel reactor (Figure 3.2-B) was constructed at Drexel University to produce larger volumes (approximately 500-1,000 ml) of biodiesel. Methanol was pumped into the reactor; the pipe delivering the methanol ran from the top to the bottom of the reactor which was enough length to vaporize the methanol inside of the reactor. The reactor was fitted with a condenser to collect the methanol/water vapor exiting the reactor. Condensate in the beginning of the reaction was typically less than 70% methanol (density >0.810 g/ml), but toward the end of the reaction, the methanol would reach 90% purity (0.796 g/ml) and could be recycled for other biodiesel reactions. The reactor was heated with electrical heating tape which enabled internal temperatures of about 120 °C. About 0.3-0.5 %m sulfuric acid catalyst was used and the reaction typically ran about 3 h. The reactor contents were re-circulated from the bottom to the top of the reactor and a sampling valve was located at the top of the reactor. Approximately 50 ml of material was drained prior to taking the sample and poured back into the top of the reactor after taking the sample. There were two drawbacks to this reactor: (1) the reaction could not be observed because the vessel was stainless steel, and (2) there are reactants at the bottom of the reactor that do not get re-circulated throughout the reaction. The crude FAME was drained from the bottom of the reactor and in initial reactions, a portion of un-reacted brown grease drained first out of the reactor after an experiment suggesting poor circulation. This problem could be fixed by partially draining the reactor in the first 30 min to ensure that there was not a bottom layer of un-reacted brown grease in the reactor.

The 4 L EFR, LLC glass reactor (Figure 3.2-C) could react approximately 3 L of brown grease using 0.3%wt sulfuric acid catalyst for 3-4 h. The reactor used a silicon oil heating bath to warm the external jacket. The temperature of the reactor could reach approximately 100-130 °C. The methanol was pumped through the heating bath to warm the methanol prior to entering the top of the reactor and was discharged at the bottom of the vessel. The reactor was also equipped with a condenser to collect the methanol/water vapor which could be recycled near the end of the reaction. Samples could be taken from the bottom of the reactor. This reactor had a similar drawback to the 1.5 L in that the bottom of the reactor should be drained to ensure the initial brown grease did not stay at the bottom of the reactor.

After esterification, the FAME was high in sulfur and still contained residual methanol, catalyst, un-reacted FFA, and acyl glycerides. To increase the yield of FAME from brown grease, transesterification may be performed to convert acyl-glycerides to FAME.

3.2.2. Transesterification

The transesterification reaction was performed in a beaker or the 4 L reactor (depending on where experiments were performed) at approximately 30 °C. The amount of potassium hydroxide catalyst required for the reaction was a sum of two amounts: (1) the amount of potassium hydroxide to neutralize any acidic components (FFA, sulfuric acid) remaining in the reactor after esterification and (2) 0.5% of the weight of brown grease as additional potassium hydroxide to act as a catalyst . To determine the amount of methanol required for transesterification, the amount of acyl glycerides was approximated as the initial brown grease mass minus the mass of FFA (assuming the FFA

was oleic acid). The methanol added to the reactor was 2.5 times the stoichiometric requirement of methanol to starting brown grease; this added an excess of methanol to ensure conversion. The transesterification reaction was run for about 2 h with constant agitation. The transesterification reaction produces glycerin by-product that is immiscible with FAME and should settle to the bottom of the reactor with the FAME on top. When a visible layer of glycerin was observed, the bottom glycerin layer was drained using a separatory funnel prior to washing of the crude biodiesel. In cases where the glycerin layer was not discernible, there was no draining and all components were water washed which would remove the glycerin in the water layer.

3.2.3. Washing

The biodiesel was usually washed with equal volume of deionized water or tap water in a separatory funnel. The water (bottom) and FAME (top) were allowed to separate and the water layer was drained. This process was repeated until the bottom water layer was clear and had a neutral pH. An example of washing crude FAME from GTW is shown in Figure 3.3.

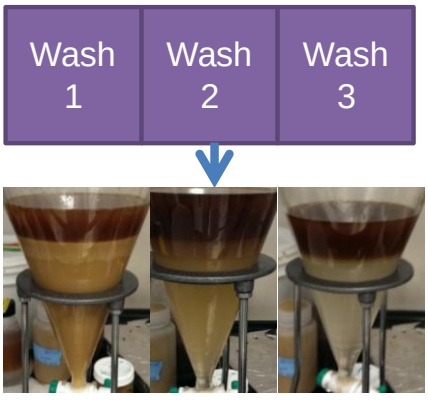


Figure 3.3: Crude fatty acid methyl ester (FAME) water washing.

The early washes of FAME produced dark, cloudy water with an acidic pH if only esterification occurred or basic pH if transesterification was performed. A common observation with brown grease FAME was that an emulsion formed during water washing that existed as a thick interfacial layer between the washed FAME (top) and wastewater (bottom). The emulsion layer shrank slowly with time, but in our experience the emulsion was layer thicker for and was more difficult to eliminate in SSG-FAME than in similar experiments with GTW-FAME. Additional information on the emulsion layer and breaking it is found in Appendix B.2. Spraying the water into the separatory funnel was effective at reducing the waiting period for the emulsion to settle.

The washed FAME was dried on a hot plate with stirring for approximately 8 h at 65-80 °C to remove water and any remaining methanol that could be present prior to vacuum distillation.

3.2.4. Vacuum Distillation

Crude biodiesel was purified using vacuum distillation. The boiling points of FAME (methyl oleate), FFA (oleic acid), and TAG (triolein) are 344, 360, and 847 ºC, respectively. The use of a vacuum during distillation helps to reduce the boiling point of the material, thus reducing energy requirements of the distillation. The vacuum distillation was performed using various temperatures and vacuum pressures; a nomograph created by Sigma-Aldrich (Sigma-Aldrich, 2016) was used to determine the atmospheric equivalent temperature (AET) of the distillation operation conditions. Figure 3.4 displays the four different vacuum distillation techniques used in this project; these described in the following sections.

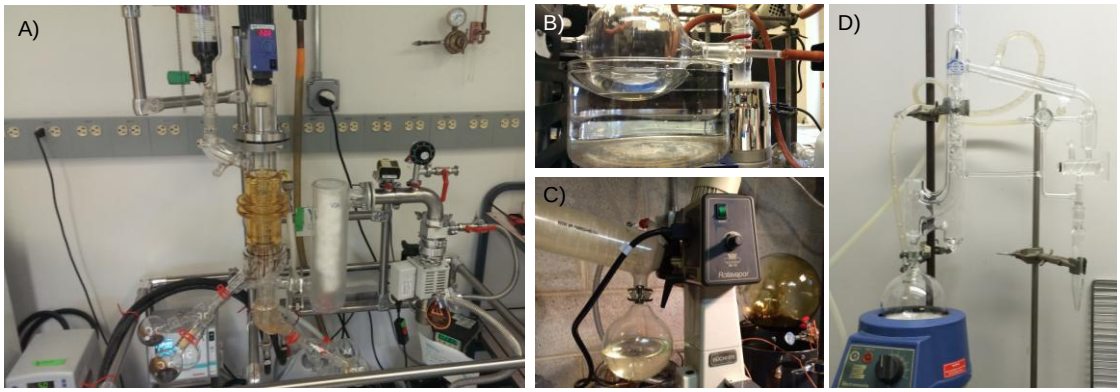


Figure 3.4: Vacuum distillation using (A) wiped film evaporator, (B) Kugelrohr distiller, (C) Rotary evaporator, and (D) Vigreaux column.

The crude FAME product after reaction, washing, and drying potentially contains FAME, un-reacted FFA, incompletely reacted acyl-glycerides, unsaponifiable lipids, and various impurities. The FAME, FFA, and acyl-glyceride fatty acids all can contain chain lengths of varying length and molecular weight. Observed chains have been 8-18 carbons and 0-3 double bonds in the lipids; the majority of the FAMEs are 16 and 18 carbons with either zero or one double bond (Long et al., 2012). The various materials and composition of carbon chain and double bonds may affect the distillation temperatures and corresponding distillate composition. In each distillation technique, there was typically a small amount of a low temperature FAME, followed by the main product middle temperature FAME, and then a high temperature FAME. The first and last distillates tended to be higher in sulfur content with the middle temperature FAME having the lowest sulfur content (Chakrabarti et al., 2008). The remaining portion that was not distilled was a viscous, dark residue that is similar to a heavy fuel oil (marine bunker fuel) and could be considered a "biobunker." The sulfur trends noted during distillation are discussed in Section 3.2.6.

3.2.4.1. Wiped Film Evaporation

The wiped film evaporator (WFE) used in the project was a Verfahrenstechnische Anlagen (VTA) standard version of the short path distillation plant (VTA, 2016) located at the USDA Eastern Regional Research Center in Wyndmoor, PA. The WFE (Figure 3.4-A and Figure 3.5) is also known as a short-path evaporator because of the small gap between the external heating wall and the internal cooling wall (VTA, 2016). A schematic of a WFE is shown in (yellow portion of Figure 3.4–A) is shown in Figure 3.5. The crude FAME flowed by gravity into the top of the heated column which had a system of rollers (wipers) that evenly spread the crude FAME in a thin film along the external wall. Some FAME evaporated and then was condensed on the cool internal column as distillate.

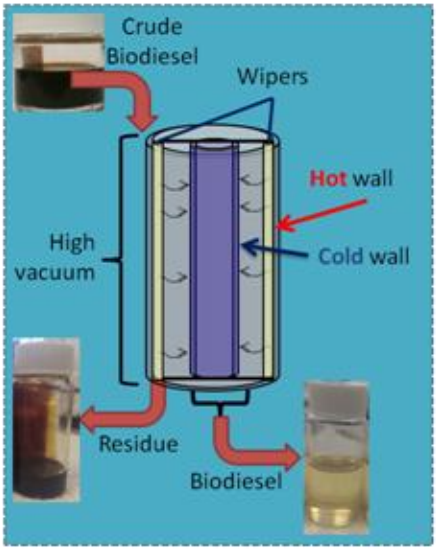


Figure 3.5 Schematic of wiped film evaporator distillation column.

This WFE used in these experiments could distill 500 ml of crude biodiesel. The column was operated using a cooling water temperature of 25 °C, vacuum pressure of 1.3

mbar, and a rotator speed of 345 RPM. The biodiesel was distilled using a two-pass system with a low temperature first pass to fractionate light sulfur FAME species (Chakrabarti et al., 2008) and a higher temperature second pass to collect the low sulfur middle temperature distillate biodiesel (Figure 3.6).

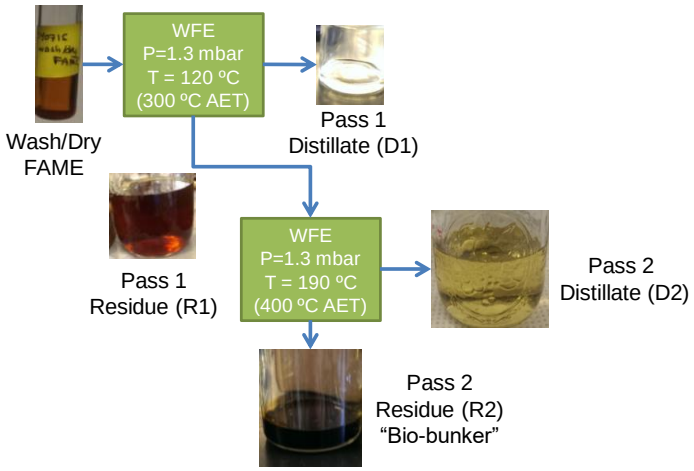


Figure 3.6: Two-pass wiped film evaporator (WFE) distillation process.

For these experiments, two passes through the WFE were used to purify the FAME samples. The first WFE pass was performed at a lower temperature of 120 °C and a vacuum pressure of 1.3 mbar (approximately 300 °C AET). The residue from this first pass was an intermediate FAME fraction and the distillate was a light fraction with high sulfur content. GC-MS characterization showed that the light fraction contained higher concentrations of shorter-chain FAME species. A second WFE pass was performed at 190 °C at 1.3 mbar (approximately 400 °C AET). The distillate from the second WFE pass was light in color and is the purified FAME distillate product. The second pass residue was the viscous, molasses-like material, biobunker.

Because of the two pass system, an experiment was performed to determine if the first pass would contaminate the distillate of the second pass. The first pass distillation was performed and split in half. Half of the first pass residue was sent through the WFE for the second pass without cleaning the apparatus and the other half was sent through the apparatus after cleaning the column with isopropanol. The cleaned second pass distillate had a sulfur content of 15 ppm S and the without cleaning distillated pass had a sulfur content of 17 ppm S. This difference was small compared to the time that would be needed to clean the column between multiple distillation experiments. The results of this experiment can be found in Appendix B.3.

The WFE performed well for vacuum distillations because it was able to keep a steady temperature and pressure throughout the experiment. However, this particular WFE was useful for small batches of distillation since the feed flask held a maximum of 500 ml. Larger batches of crude biodiesel would need to be divided which could be time consuming.

3.2.4.2. Kugelrohr Distillation

The Kugelrohr distillation experiments were performed in the Drexel University Chemistry Department (Figure 3.4-B). The goal of Kugelrohr distillation was to perform a temperature study on the distillate to analyze distillate yield and sulfur contents. A schematic diagram of the Kugelrohr Distillation is shown in Figure 3.7. The collection flask was rotated in an ice-cold water bath to condense the vapor in the flask; if the ice bath was too cold, the distillate solidified in the collection flask.

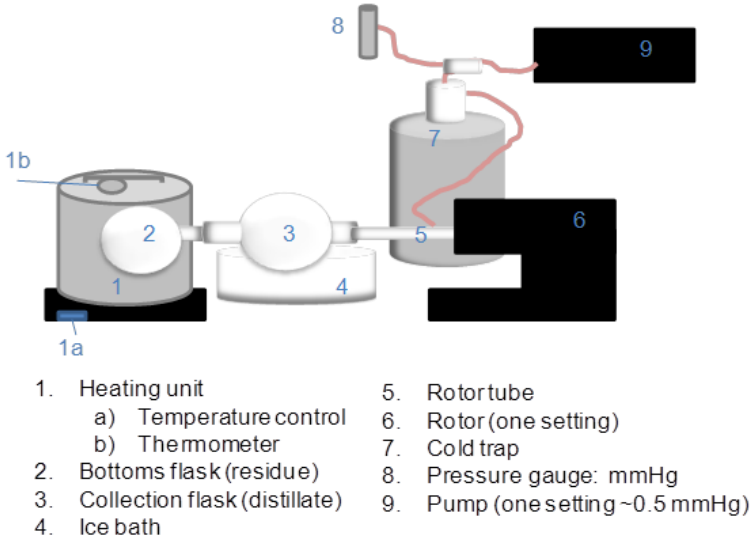


Figure 3.7: Schematic of Kugelrohr distillation apparatus.

The vacuum pressure was about 1 mbar and the temperature was increased between 150-200 ºC, the maximum temperature of the heating unit. The first distillate was observed at around 170 °C but condensed in the neck of the collection flask. The condensate was collected in the collection flask at temperatures around 180 °C. Kugelrohr distillation was originally meant to collect samples of biodiesel at different temperatures; however, the maximum temperature of the heater was 200 °C and the sensitivity of the actual temperature was ± 3 °C, which limited the number of temperatures that distillate collection could occur.

3.2.4.3. Rotary Evaporation

The rotary evaporator was operated at EFR, LLC. The bottom flask on the right in Figure 3.4-C was heated and rotated in an oil bath with a vacuum of 1-3 mbar and cooling water ran through the condensing column. Condensate first formed at lower temperatures around 120 °C and was collected flasks were switched when condensate

slowed. This fraction could be comparable to the first pass of the WFE. The temperature increased to 190 ºC and distillate was collected which could be comparable to the second pass of the WFE. The rotary evaporator worked well for larger volumes of FAME (1 L). The vacuum system was not as stable as the WFE and there was occasionally knocking in the bottom flask that would cause a large burst of crude FAME to enter the condensing tube.

3.2.4.4. Vigreaux Column Distillation

The Vigreaux column is owned by Drexel Chemical and Biological Engineering Department. The bottom flask was heated and sent through a staged distillation column with an attached condenser at the top (Figure 3.4-D). The vacuum was approximately 1-3 mbar and the temperature ranged from 140-165 °C. The sampling valve made collection of biodiesel samples easy despite the vacuum; as the temperature was increasing in the column, 10 ml samples were taken throughout the distillation experiment.

3.2.5. Biodiesel Quality

3.2.5.1. High Performance Liquid Chromatography

Samples throughout the biodiesel process were also evaluated using high performance liquid chromatography (HPLC) to observe qualitative changes in the components. The sample was injected into the column at a concentration which overloaded the FAME peaks at 15 mg sample/ml solvent (99.3%Hexane:0.6%Isopropanol:0.1% Acetic Acid) which enabled more-sensitive detection of other components such as acyl-glycerides. The solvent gradient method used was not calibrated to determine exact composition of each of the components. Table 3.2

displays elution times of reference compounds for the HPLC method; the table is color-coded for ease of identification of the corresponding peaks in the HPLC chromatograms. For example, a brown grease lipid sample should have a large peak at 2.7-3.5 min (orange) indicating a large amount of FFA present in the sample. After esterification, the sample should show a decrease in the FFA peak and a new peak at 1.9-2 min (yellow) should appear representing FAME.

Table 3.2: Elution times for reference compounds with the higher performance liquid chromatography method.

Time, min	1.3	1.9-2	2.7-3.5	6	7.3	7.9	10.6	25	30-35
Compound	Sterol ester	FAME	FFA	TAG	Free sterol	DAG	MAG	Phospho-lipid	Lyso-phospho-lipid

However, there is the possibility that some compounds present in brown grease may elute at the same time as some of these peaks. Oxidized fatty acids may elute at the same time as sterol esters, but HPLC combined with mass spectroscopy could be utilized to try to identify these discrepancies (Moreau & Hicks, 2006).

3.2.5.2. Sulfur Measurements

The sulfur content was measured using a ThermoScientific TS 3000 Total Sulfur Analyzer and TS-UV Module total sulfur detector on a 0-50 ppm S setting using method TSUV_E_Manual_Liquids1075. Calibrations were performed using triplicate testing of standard biodiesel samples from AccuStandard spiked with 7.5, 15, 30, and 50 ppm S. Some biodiesel samples were analyzed on a 0-200 ppm S setting and calibrations were performed using standards spike with 15, 30, 50, and 200 ppm S.

3.2.5.3. Iowa Central ASTM Testing

Several samples were sent to Iowa Central for critical specification testing. These tests were performed in accordance with ASTM D6751 at Iowa Central Laboratories (ASTM, 2015).

3.2.6. Statistical Analysis

Statistical analysis was performed using IBM SPSS Statistics 23 (IBM, 2015). 1-tailed Pearson correlations were used; the Pearson coefficient indicates the trend of the correlation (positive or negative) and the significance indicates the strength of the correlation. Pearson values above 0.05 are not considered significant; values below 0.05 and above 0.01 are considered weakly significant; and values below 0.01 are considered significant. One-way ANOVA (comparison of means) was also performed to determine the statistical significance between distillation equipment. The parameters studied for correlations are shown in Table 3.3.

Table 3.3: Distillation correlation parameters.

	Parameter	Description
Distillation Conditions	Vacuum Pressure (mbar)	Pressure during distillation
	Temperature (°C)	Temperature during distillation
	AET Temperature (°C)	Atmospheric equivalent temperature of distillation conditions
Yield	Distillate Yield (%)	Yield of distillate from amount of crude biodiesel into distillation
Sulfur Content	Distillate Sulfur (ppm S)	Sulfur content of distillate biodiesel
	Sulfur Reduction from Crude (%)	Percent sulfur reduction of distillate biodiesel to crude biodiesel
	Sulfur Reduction from Lipids (%)	Percent sulfur reduction of distillate biodiesel to starting lipids
TAN	Distillate Total Acid Number (mgKOH/g)	Total acid number of distillate biodiesel

The boxes are colored to identify similar parameter groupings. Distillation conditions (temperature and pressure) are shown in blue; yield of distillate is shown in red; distillate sulfur contents are shown in green; and total acid number of distillate is shown in purple.

3.3. Results

3.3.1. Biodiesel Conversion

Figure 3.8 is a visual representation of amounts of material at each process stage defined by mass yield. This process assumed that there was 95% conversion of brown grease to crude FAME and that the purification process had a 90% yield.

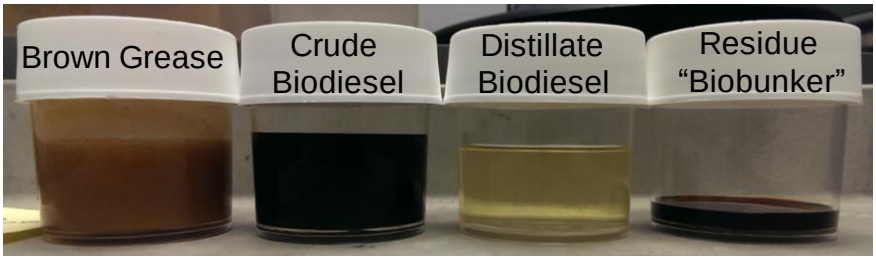


Figure 3.8: Biodiesel production from brown grease shown by yields at each stage.

The next two sections describe two particular experimental results for biodiesel produced from GTW and SSG. These two experiments were chosen to report because of the visual documentation of each process stages. Also, these experiments were performed to prepare biodiesel samples using identical processing conditions to distill in the WFE on the same visit to the USDA.

3.3.1.1. Biodiesel Produced from Grease Trap Waste

GTW brown grease lipids were converted into FAME, washed, dried, and purified. This particular experiment in Figure 3.9 was performed to analyze vinegar

washed lipid conversion, so two esterification reactions were performed on lipids with and without pretreatment. Samples were taken to determine the FFA content, yield, and sulfur content throughout the process.

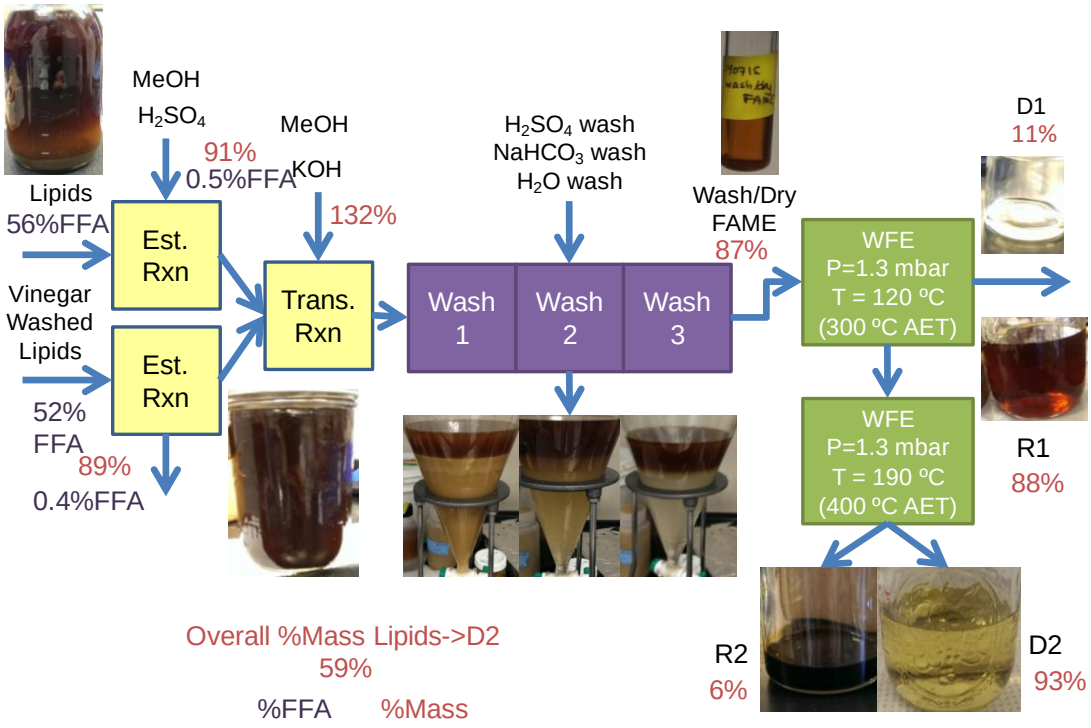


Figure 3.9: Grease trap waste biodiesel production showing free fatty acid (FFA) content (purple) and yield at each process stage (red).

In this specific experiment, two batches of GTW lipids were esterified in the bubble column reactor with methanol and 0.5% mass sulfuric acid. One batch used lipids "as-is" and the other batch used lipids that were washed with vinegar for 1 h. No noticeable difference between the two esterification reactions was observed. Since the starting material was ~54% FFA (which was a low FFA content as determined in the longitudinal study), the two esterified materials were combined and transesterified to

convert any triglycerides to FAME. No apparent separation of glycerol and FAME was observed so the entire mixture was washed (shown by the increase in %mass seen above). The crude FAME was washed once with an acidic water wash, once with a 1% mass sodium bicarbonate ($NaHCO_3$), and once with only a water wash and afterwards dried overnight. Wash/Dry FAME was purified using a two-pass method in the WFE. The first pass was run at 1.3 mbar and 115 °C (300 °C AET) and a second pass was run at 1.3 mbar and 190 °C (400 °C AET). Residue (R) represents the high boiling point temperature liquid that did not distill while distillate (D) represents the low boiling point temperature liquid that vaporizes and is condensed.

The sulfur concentration and mass are shown in Table 3.4.

Table 3.4: Biodiesel from grease trap waste sulfur content by process stage.

Stage of Reaction	Concentration Sulfur, ppm S	Mass Sulfur, mg S
Lipid 1	92	15
Lipid 2	99	13
Total Lipid	96	28
Esterified FAME 1 from Lipid 1	167	21
Esterified FAME 2 from Lipid 2	181	23
Total Esterified FAME	175	44
Transesterified FAME	94	32
Wash/Dried FAME	65	15
Wash/Dried FAME into WFE Pass 1	65	14
Pass 1 300 °C AET Residue (R1)	75	14
Pass 1 300 °C AET Distillate (D1)	22	0.5
R1 into WFE Pass 2	75	14
Pass 2 400 °C AET Residue (R2)	393	4
Pass 2 400 °C AET Residue (D2)	10	2

A sulfur balance was performed to determine if sulfuric acid had an effect on the sulfur content of FAME. While the sulfur content increased by about 16 mg total in the two esterification reactions, the increase was not significant considering 490 mg S was introduced to the reaction through the sulfuric acid catalyst. In addition, the sulfur content was reduced during the washing stage indicating that the sulfuric acid is removed during washing and has no impact on the sulfur content of the final distillate. After distillation, the biodiesel met ASTM sulfur standards at 10 ppm S.

The HPLC results (Figure 3.10) show the transformation of FFA in the lipids (A1 and A2) to FAME after esterification (B1 and B2). While the FFA peak appears large in the post-esterification diagrams indicating the presence of a substantial amount of FFA, the response factor of the FFA components in HPLC detector is known to be larger than FAME; so the amount of FFA is smaller than it appears by the peak area. After transesterification (C) and washing/drying (D), FAME was the largest peak present in the samples. The residue in first distillation stage (E1) showed a presence of FAME and sterols peaks while the distillate (E2) showed a presence of FAME and sterol esters. The residue in the second distillate stage (F1) showed a presence of almost all components especially at the higher elution times. The distillate of the second pass (F2) was the biodiesel product which showed primarily FAME and some sterol esters.

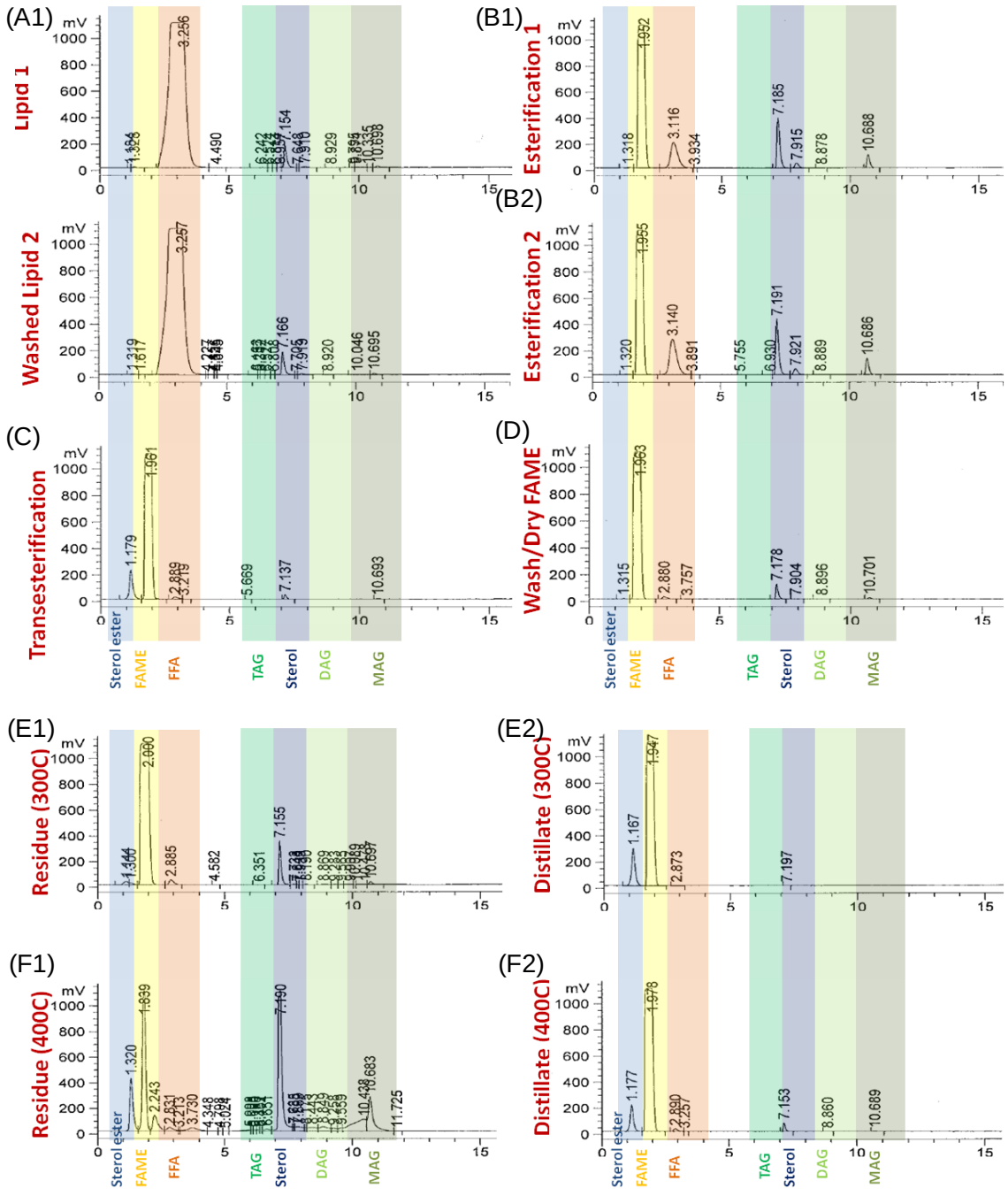


Figure 3.10: High performance liquid chromatographs by grease trap waste process stage: (A) brown grease lipids, (B) esterified fatty acid methyl ester (FAME), (C) transesterified FAME, (D) washed/dried FAME, (E) low temperature first pass distillation, and (F) higher Temperature second pass distillation.

While peaks are present at the sterol and sterol ester times, they may not actually be sterols or sterol esters. After talking with researchers at USDA, oxidized FFAs and FAMEs as well as wax-esters could appear at the same elution times as sterols and sterol esters.

3.3.1.2. Biodiesel Produced from Sewage Scum Grease

SSG brown grease lipids were converted into FAME, washed, dried, and purified as shown in Figure 3.11. This particular experiment was the first reaction using SSG brown grease as a feedstock.

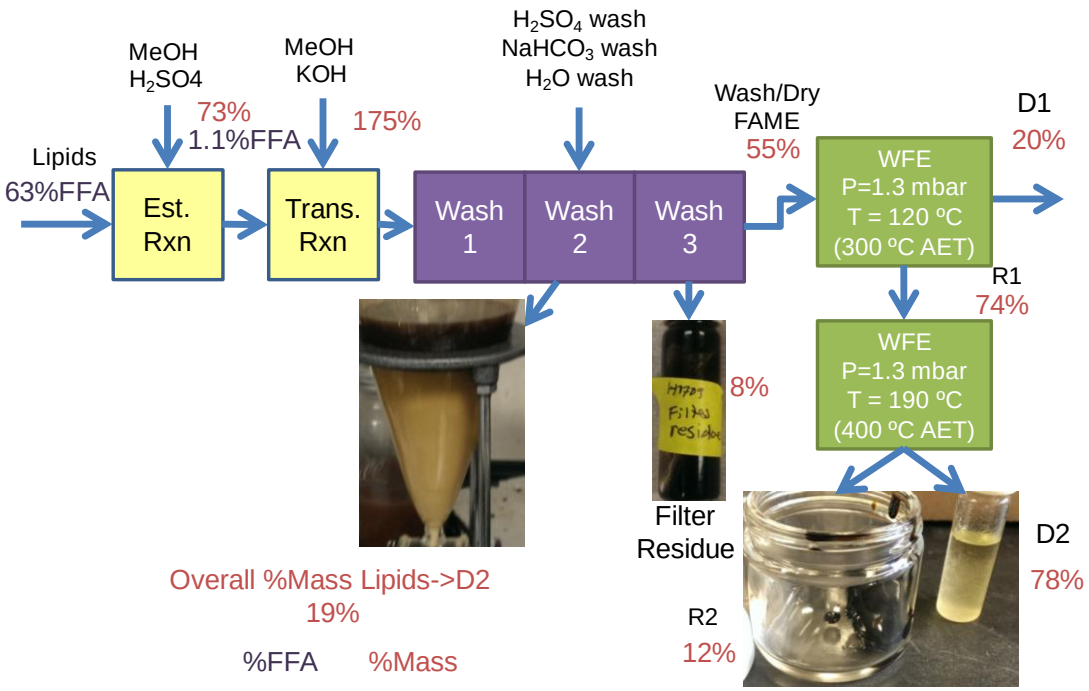


Figure 3.11: Sewage scum grease biodiesel production showing free fatty acid (FFA) content (purple) and yield at each process stage (red).

This batch of SSG lipids were converted in the same manner as GTW described in the previous section except this process did not include vinegar washed lipids. The brown

grease was esterified and transesterified; FAME was washed, dried, and distilled using the same WFE two-pass system.

There were some differences of SSG biodiesel distillation compared to GTW biodiesel distillation. The residue from the second pass, R2, solidified in the line and the WFE had to be heated with a heat gun for it to flow into the collection flask. After cooling, the distillate was cloudy and appeared to have a small amount of crystallization. It is possible that the same distillation temperatures are not suitable for SSG distillation. Solidification could occur if the FAME is composed of shorter chain fatty acids or degree of saturation, their melting and boiling points would be slightly lower than a longer chain molecule.

A sulfur balance was performed to track the sulfur content throughout the biodiesel production. The sulfur concentration and mass of sulfur are shown in Table 3.5.

Table 3.5: Biodiesel from sewage scum grease sulfur content by process stage.

Stage of Reaction	Concentration Sulfur, ppm S	Mass Sulfur, mg S
Lipid	429	42
Esterified FAME	N/A	N/A
Transesterified FAME	87	11
Wash/Dried FAME	259	10
Wash/Dried FAME into WFE Pass 1	259	10
Pass 1 300 °C AET Residue (R1)	461	12
Pass 1 300 °C AET Distillate (D1)	49	0.4
R1 into WFE Pass 2	461	11
Pass 2 400 °C AET Residue (R2)	439	1
Pass 2 400 °C AET Residue (D2)	87	1

The sulfur trends are similar to the GTW-biodiesel production. The initial lipids are high in sulfur content but washing is able to remove not only the sufluric acid that was added, but also some of the starting sulfur. The transesterfied FAME concentration appeared low (87 ppm S), however this sample had a large amount of methanol that diluted the sample. Unlike GTW, the final SSG distillate has a high sulfur concentration which does not pass ASTM specifications. The first pass distillate also had a lower sulfur content (49 ppm S) than the second pass distillate (87 ppm S) which supports the theory mentioned in the last section that the temperature conditions were too hot for the FAME.

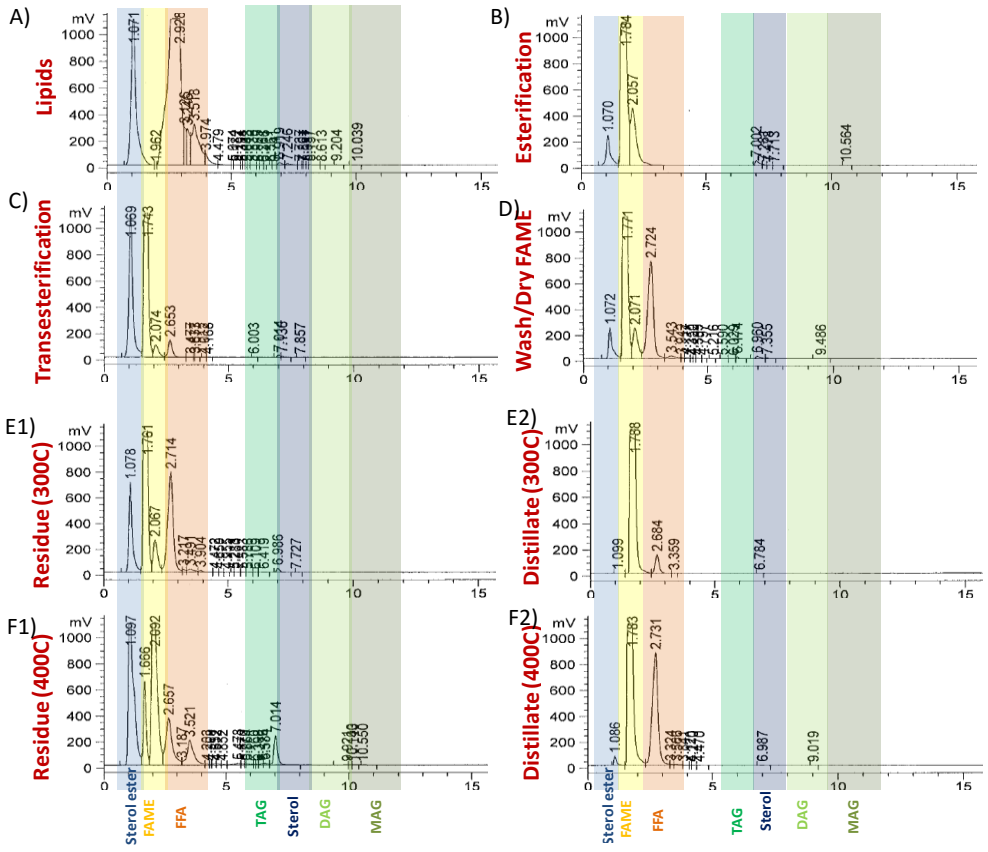


Figure 3.12: High performance liquid chromatographs by sewage scum grease process stage: (A) brown grease lipids, (B) esterified fatty acid methyl ester (FAME), (C) transesterified FAME, (D) washed/dried FAME, (E) low temperature first pass distillation, and (F) higher Temperature second pass distillation.

The HPLC results (Figure 3.12) shows the transformation of FFA in the lipids (A) to FAME after esterification (B). After transesterification (C) and washing/drying (D), FAME was the largest peak present in the samples. The residue of the first pass (E1) had small peaks detected throughout the time scale but had the biggest peaks at the elution times indicating FAME, FFA, and sterol esters. The distillate of the first pass (E2) showed a large FAME peak with only another small FFA peak. The second pass residue (F1) had peaks at most of the elution times but had the highest peaks where FAME, FFA, and sterol esters are detected. The second pass distillate (F2) showed FAME detection, however there is a second large peak detecting FFA; this FFA peak was not detected in the first pass distillate (E2) which could indicate that the distillation was hot enough to distill FFA.

3.3.2. ASTM Testing

The FAME sent for ASTM testing at Iowa Central generally passed all of the tests except for (1) oxidative stability, (2) total acid number, and (3) sulfur content. Results of the ASTM tests are shown in Table 3.6. The oxidative stability can be corrected by using an antioxidant in the distilled FAME. The total acid number can be reduced using a basic wash or Magnesol® (a magnesium silicate adsorbent). The difficult test to pass is the sulfur content as distillation alone has not been able to consistently meet the ASTM specification.

Table 3.6: ASTM D6751 biodiesel testing results.

		Limits		GTW FAME (9 Batches)				SSG FAME (1 Batch)			
ASTM Specification	**Unit**	**Max**	**Min**	**Average**	**Stdev**	**# Pass**	**# Fail**	**Average**	**Stdev**	**# Pass**	**# Fail**
Sulfur tested at USDA	**PPM**	**15**		**17**	**21**	**2**	**7**	**76**		**0**	**1**
Critical Test Package at ICFTL											
Sulfur (ICFTL)	**PPM**	**15**		**25.6**	**19.4**	**1**	**8**	**78.1**		**0**	**1**
Total Acid Number	**mg KOH/g**	**0.5**		**0.73**	**0.83**	**5**	**4**	**0.42**		**1**	**0**
Oxidation Stability	**hours**		**3**	**0.2**	**0.5**	**0**	**9**	**1.4**		**0**	**1**
Flash Point	C		93	153.3	18.1	8	0	142.5		1	0
Alcohol Control Methanol	C	0.2		0	0	2	0	0		1	0
Alcohol Control Flash Point	C		130	164.2	9.9	5	0	142.5		1	0
Water & Sediment	% vol	0.05		0.0017	0.0029	3	0	<0.005		1	0
Cloud Point	C	report		3.1	3.5			13		1	0
Cold Soak Filterability	sec.	360	*	109.7	7.1	4	0	100		1	0
Free Glycerin	% mass	0.02		0.0071	0.0078	9	0	0.019		1	0
Total Glycerine	% mass	0.24		0.0538	0.0536	9	0	0.02		1	0
Monoglycerides	% mass			0.1756	0.1976			0.004		1	0
Diglycerides	% mass			0.0078	0.0052			0		1	0
Triglycerides	% mass			0	0			0		1	0
Visual Inspection	haze	2		1	0	8	0	1		1	0
ASTM Specification	**Unit**	**Max**	**Min**	**GTW FAME (1 Sample)**							
Full Test Package Additional Tests at ICFTL											
Kinematic Visccosity	mm2/s	6	1.9	4.404		1					
Sulfated Ash	% mass	0.02		0		1					
Copper Corrosion	code	3		1A		1					
Carbon Residue	% mass	0.05		0		1					
Distillation at 90%	C	360		352.3		1					
Calcium & Magnesium	PPM	5		0.1		1					
Phosphorous	% mass	0.001		0		1					
Sodium & Potassium	PPM	5		0		1					
Cetane			47	54.9		1					

3.3.3. Sulfur Contents

3.3.3.1. Sulfur Contents throughout Sulfur Processing

The distillate FAME production from both GTW and SSG has shown sulfur reduction throughout the conversion process. The histogram in Figure 3.13 shows the sulfur content of brown grease, crude biodiesel, and distilled biodiesel from experiments in this project. The histogram displays ranges of sulfur content in the samples and how sulfur content changes during processing starting from brown grease (right) to distilled

FAME (left). The dashed vertical red line represents the 15 ppm S ASTM specified sulfur limit for biodiesel.

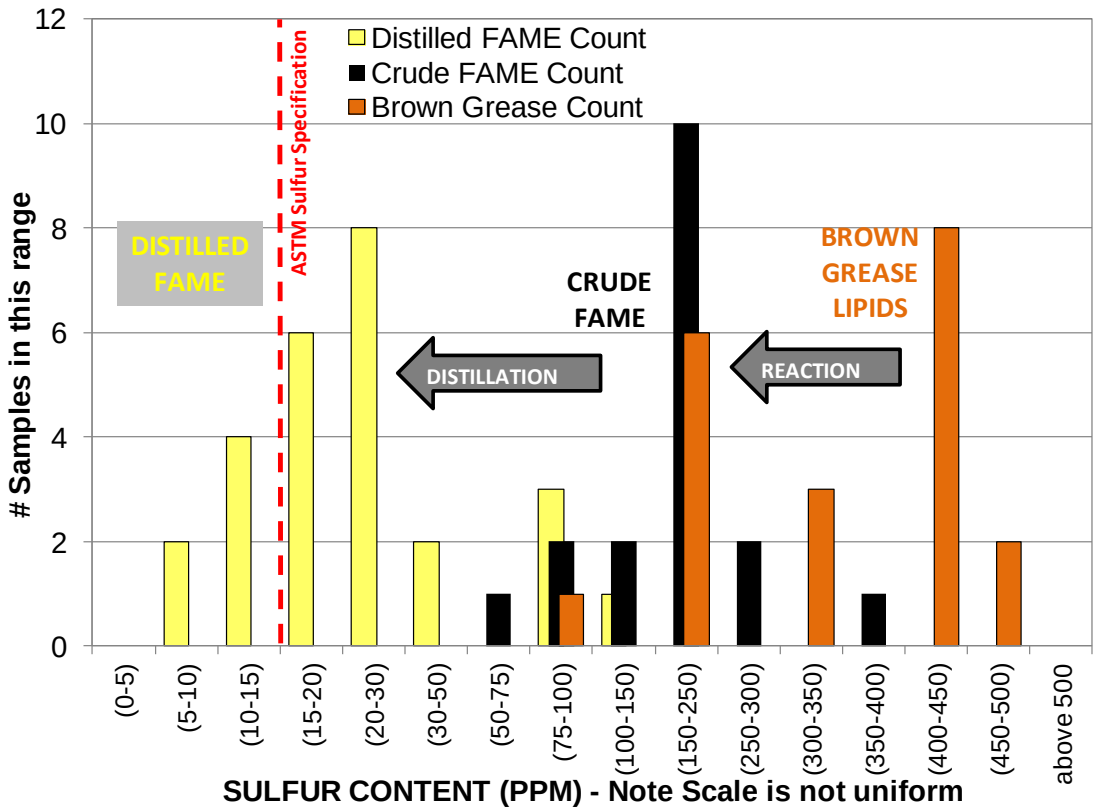


Figure 3.13: Histogram of sulfur concentration throughout biodiesel production.

Brown grease lipids (light brown) had 50% of samples that were between 400-500 ppm S. The second highest range with 30% of brown grease samples were between 150-250 ppm S. There was one GTW brown grease sample with 96 ppm S which was unusually low for brown grease. Crude FAME (dark brown) has 55% of samples that were between 150-250 ppm S; this showed about a 50% reduction in sulfur just through the reaction of the brown grease and washing of the FAME. Because sulfuric acid was added, there was concern that the sulfuric acid could increase the sulfur content of the material, but it

appeared that the sulfuric acid washed out when the FAME was washed. The distilled FAME (yellow) had 56% of samples that were between 15-30 ppm S, which was approximately 75-93% sulfur reduction from brown grease lipids. Figure 3.13 contains both SSG and GTW combined data; however, SSG generally had higher sulfur contents than GTW for brown grease lipids and final distillate.

Table 3.7 shows the separated GTW and SSG sulfur content ranges. Residue refers to the biobunker or the un-distilled portion of the starting crude FAME. Condensate refers to the first pass distillate through the WFE, or the light (low boiling point) sulfur containing FAMEs. Distillate refers to the potential product biodiesel (distilled FAME).

Table 3.7: Sulfur concentration throughout biodiesel production.

Process Stage	SSG Avg, ppm S	SSG Range, ppm S	GTW Avg, ppm S	GTW Range, ppm S
Brown Grease Lipids	453	429-474	307	(96) 153-427
Washed FAME	255	143-364	171	(65) 80-282
Residue	829	439-1575	1227	(393) 183-5371
Condensate	195	32-504	127	(22) 32-504
Distillate	66	36-87	28	(10) 5.8-107
Sulfur Reduction: Lipids to Washed FAME	44%	23-67%	44%	34-48%
Sulfur Reduction: Lipids to Distillate	85%	82-92%	91%	75-96%
Sulfur Reduction Washed FAME to Distillate	74%	75-76%	84%	62-93%

(x) outlier: unusually low GTW sample

GTW sulfur content tended to be lower than that of SSG throughout the FAME production process. This observation is most notable in the final distillate sulfur contents where SSG had 76-87 ppm S and GTW had 12-27 ppm S. However, the condensate

value (first pass/low temperature distillation) of SSG was less than GTW and the SSG second pass/high temperature distillation. This result could mean that SSG requires different distillation temperatures compared to GTW. A comparison of means was performed and there was no statistically significant difference between GTW and SSG samples. Results of the comparison of means are shown in Appendix B.6.1. These results were based off of three samples of SSG biodiesel and twenty-four GTW samples; therefore, more SSG experiments should be performed to test whether or not these initial observations of sulfur difference are significant.

The sulfur results were similar to reported distillation sulfur contents of crude FAME produced from wastewater treatment plant greases. Chakrabarti et al. showed a range of pre-purification biodiesel 180-391 ppm S (Chakrabarti et al., 2008). Gardner et al. reported sulfur contents from 160-328 ppm S; however, it is unclear whether or not these samples of crude FAME were washed (Gardner et al., 2013). A majority of samples were reported around mid-300 ppm S in these reports; the washed FAME in this research showed lower average sulfur content compared to that of the reported biodiesel. This result could mean that the Drexel/Environmental Fuel Research, LLC process is more effective at reducing the sulfur content through the esterification and washing of biodiesel. Two notable reaction differences are reaction temperature and catalyst usage. This research uses an elevated temperature to bubble in vaporous methanol which could promote sulfur stripping throughout the biodiesel reaction. Gardner et al. and Chakrabarti et al. reported using approximately 7 %mass sulfuric acid to FFA (Chakrabarti et al., 2008; Gardner et al., 2013) while this research also uses less sulfuric

acid at approximately 0.4 %mass sulfuric acid to FFA. However, sulfuric acid is washed out with water so this difference may not affect the overall sulfur content of biodiesel.

3.3.3.2. Distillation Experiments Correlations

The temperature of the distillation is the easiest variable to control during the distillation process because the vacuum pressure is usually limited to the type of equipment being used. The temperature of the distillation appeared to have an effect on the sulfur content of the distillate; therefore, an experiment was performed using the WFE. Figure 3.14 shows the HPLC results and sulfur contents of each stage of the FAME production process.

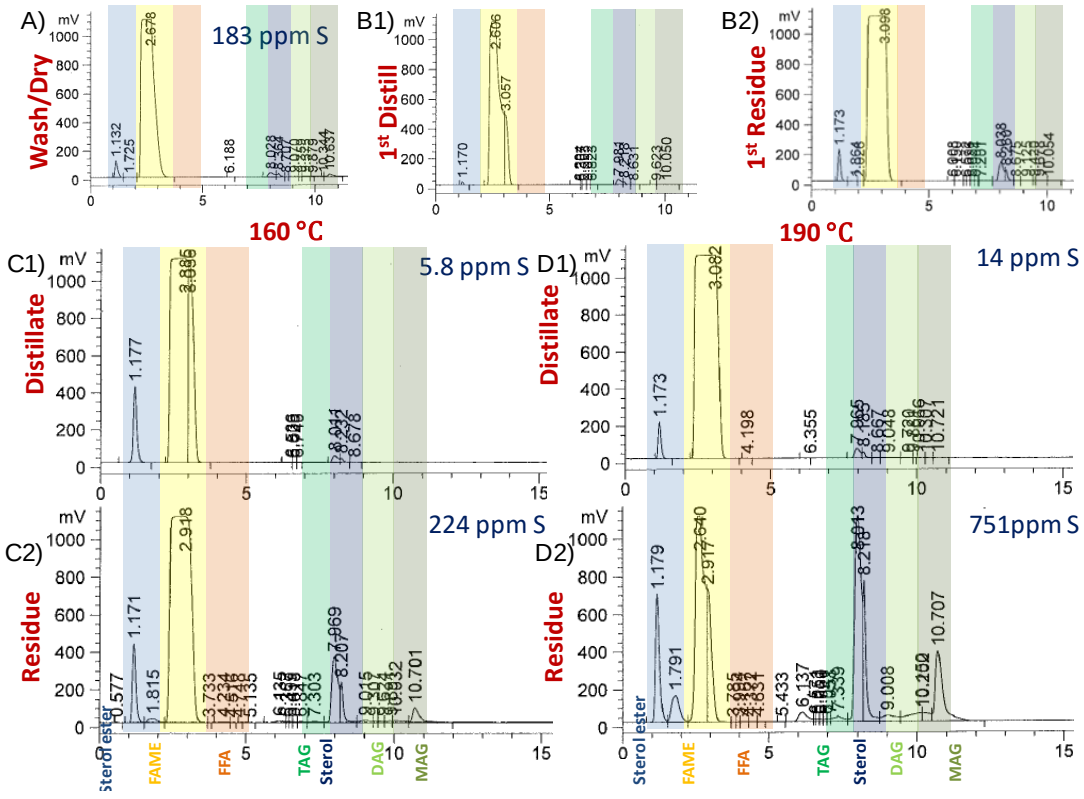


Figure 3.14: High performance liquid chromatographs for 2nd distillation temperature: (A) start crude, (B1) 1st pass distillate, (B2) 1st pass residue, (C1) low temperature 2nd pass distillate, (C2) low temperature 2nd pass residue, (D1) high temperature 2nd pass distillate, and (D2) high temperature 2nd pass residue.

The wash/dry crude biodiesel was initially 183 ppm S. The first pass condensate (distillate) sulfur content was not recorded due to time constraints. The residue from the first pass was split in half to run the second pass at two different temperatures. The first half was run through at 160 °C, 1 mbar (360 °C AET) and the second half was run through at 190 °C, 1 mbar (400 °C AET). The sulfur content at the lower temperature was 5.8 ppm S and at the higher temperature was 14 ppm S. While the sulfur content was less for the lower second pass temperature, the yields was also lower. The distillate yield for the second pass was 94% for the higher temperature and 55% for the lower temperature.

Because of the variability of crude biodiesel sulfur content and the distillation operating conditions, it is difficult to compare all of the different distillation experiments that have been performed to analyze trends in the purified FAME sulfur content and yield. Therefore, the reaction conditions and the distillate sulfur contents were normalized to try to compare each individual distillation experiment. The operating pressure and temperature were translated to the AET. The sulfur reduction represents the percent reduction between the crude biodiesel and the distillate biodiesel. The yield represented the mass of distillate divided by the mass of crude biodiesel into the distillation; for WFE this was the mass of distillate divided by the mass of crude biodiesel into the first pass. Appendix B.5 contains information on all of the distillation experiments performed. Figure 3.15 shows summarized results of the sulfur reduction and distillate yield compared to the atmospheric equivalent temperature of distillation conditions.

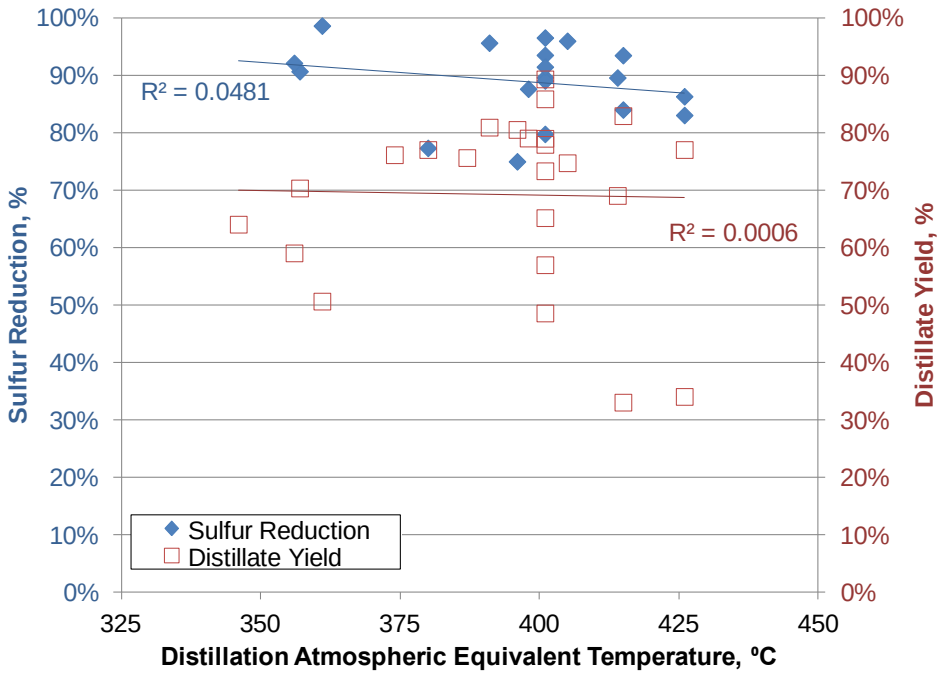


Figure 3.15: Sulfur content and distillate yield compared to atmospheric equivalent temperature of distillation operation for all distillation experiments conducted.

The sulfur and yield both have a relatively horizontal trend over the AET showing that the sulfur reduction is independent of distillation temperature. The lack of trend between sulfur content, yield, and distillation AET is further shown in the SPSS correlation results in Table 3.8.

Table 3.8: Correlations in distillation experiments.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Vacuum Pressure (mbar)	**Sulfur Reduction from Lipids (%)**	-0.558**	0.007	19	Sulfur reduction from starting lipids inversely related to distillation pressure	SIG.
Vacuum Pressure (mbar)	**Distillate Sulfur (ppm S)**	-0.414*	0.022	24	Sulfur content of distillate biodiesel inversely related to distillation pressure	WEAKLY SIGNIFICANT
Temperature (°C)	**Distillate Sulfur (ppm S)**	-0.384*	0.032	24	Sulfur content of distillate biodiesel inversely related to distillation temperature	

The correlation results showed one significant trend between vacuum pressure and the sulfur reduction from the starting lipid sulfur content. There were two weakly significant correlations between the distillate sulfur content and vacuum pressure and the distillate sulfur content and temperature. AET was determined using the vacuum pressure and operating temperature; however, AET was not correlated to the distillate sulfur content.

A comparison of averages was performed using one-way ANOVA to determine if there were any statistically significant differences of distillation equipment type or brown grease feedstock. The results showed that there were no significant differences between the types of distillation performed. These results are shown in Appendix B.6.2.

3.3.3.3. Vigreaux Distillation Correlations

Vigreaux distillation allowed for easier sampling at various temperatures throughout the distillation process which made analyzing temperature and pressure correlations on a single sample easier. Figure 3.16 shows the GTW and SSG distillate biodiesel (FAME) sulfur content and total acid number throughout the distillation.

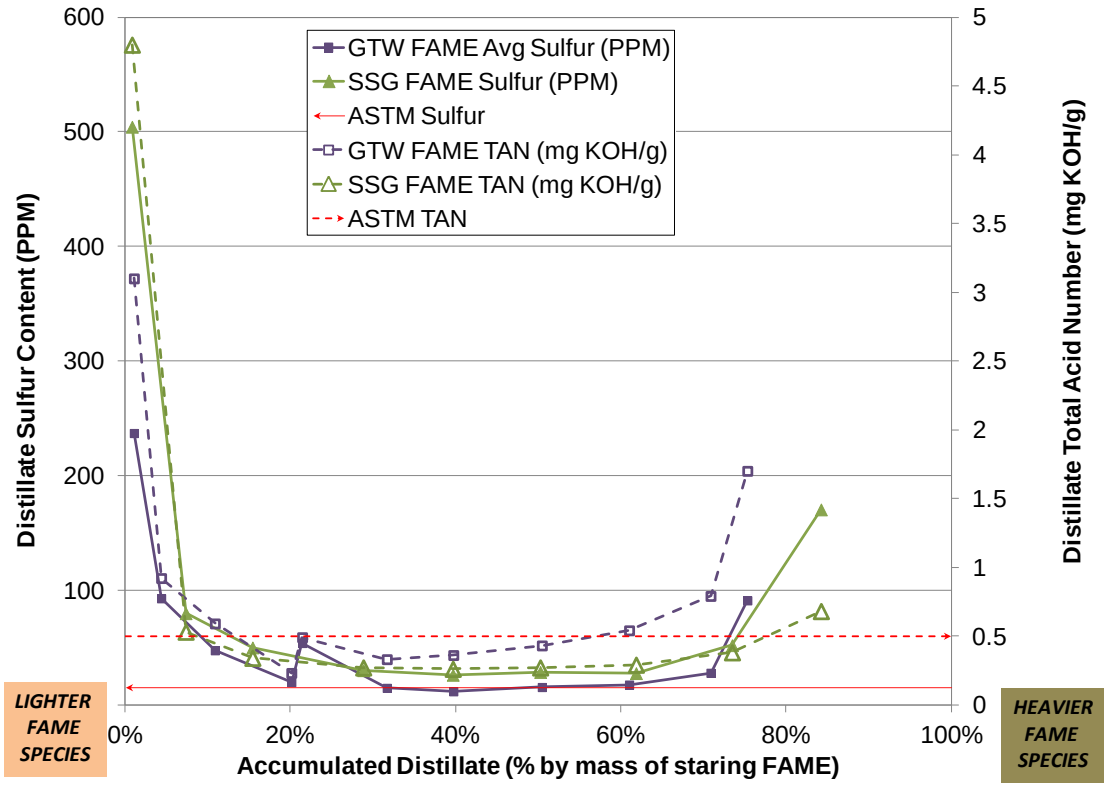


Figure 3.16: Distillate sulfur content and total acid number (TAN) throughout Vigreaux distillation experiment.

The distillate sulfur content and TAN for both GTW and SSG had similar trends over the accumulated distillate. At the start of distillation, there was a high sulfur content and TAN which was similar to the low temperature first pass during WFE. As the distillation continued there was a range of low-sulfur, low-TAN (20%-70%) accumulated distillate. In this range, most samples were lower than the ASTM standard TAN value (0.5 mgKOH/g; marked by dotted red line). For samples of GTW, there were a few samples in this range that were lower than the ASTM standard sulfur content (15 ppm S; marked by solid red line). When distillate accumulation slowed at the end of distillation (temperature increases), the sulfur contents and TAN increased.

A trend between TAN and sulfur content was observed throughout the Vigreaux distillation. Figure 3.17 shows the TAN of distillate compared to the sulfur content.

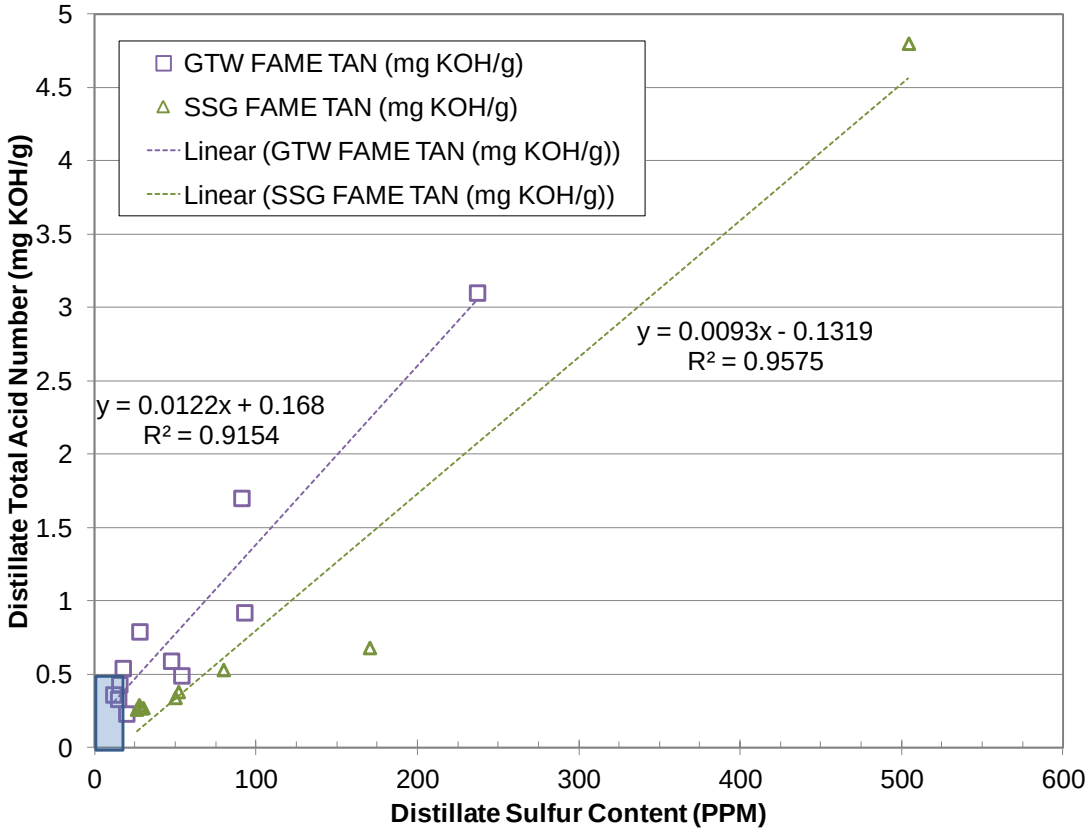


Figure 3.17: Vigreaux distillate total acid number compared to distillate sulfur content.

There was a positive correlation between sulfur content and TAN for both GTW and SSG distillate. A straight line was fit to each data set and both R-squared values showed strong correlation between the variables. To determine if these correlations were statistically significant, SPSS bivariate correlation testing was performed for the Vigreaux distillation experiments for GTW and SSG samples.

Table 3.9: Correlations in grease trap waste distillate from Vigreaux distillation.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Distillate Sulfur Content	Distillate TAN	.957**	1.99E-06	11	Sulfur content is positively correlated to TAN	SIGNIFICANT
Distillate TAN	AET	-.809**	1.27E-03	11	TAN is inversely correlated to atmospheric equivalent temperature of distillation operation conditions	
Distillate TAN	Temperature	-.722**	6.03E-03	11	TAN is inversely correlated to operational temperature of distillation	
Accumulated Distillate	AET	.649*	1.53E-02	11	Distillate accumulated is correlated to operational temperature of distillation	WEAKLY SIGNIFICANT
Distillate Sulfur Content	AET	-.649*	1.54E-02	11	Sulfur content is inversely correlated to atmospheric equivalent temperature of distillation operation	
Accumulated Distillate	Temperature	.588*	2.87E-02	11	Distillate accumulated is correlated to operational temperature of distillation	
Distillate Sulfur Content	Temperature	-.573*	3.28E-02	11	Sulfur content is inversely correlated to operational temperature of	

** Significant at 0.01 level
* Significant at 0.05 level

Table 3.10: Correlations in sewage scum grease distillate from Vigreaux distillation.

Parameter	Parameter	Pearson Correl.	Sig. (1-tailed)	N	Relevance	
Distillate Sulfur Content	Distillate TAN	.979**	2.35E-06	9	Sulfur content is positively correlated to TAN	SIGNIFICANT
Distillate TAN	AET	-.962**	1.66E-05	9	TAN is inversely correlated to atmospheric equivalent temperature of distillation operation conditions	
Distillate Sulfur Content	Vacuum Pressure	.944**	6.40E-05	9	Sulfur content is correlated to vacuum pressure of distillation	
Distillate Sulfur Content	AET	-.919**	2.29E-04	9	Sulfur content is inversely correlated to atmospheric equivalent temperature of distillation operation conditions	
Distillate TAN	Temperature	-.900**	4.68E-04	9	TAN is inversely correlated to operational temperature of distillation	
Distillate TAN	Vacuum Pressure	.900**	4.73E-04	9	TAN is correlated to vaccum pressure of distillation	
Distillate Sulfur Content	Temperature	-.838**	2.40E-03	9	Sulfur content is inversely correlated to operational temperature of	
Accumulated Distillate	Temperature	.794**	5.28E-03	9	Distillate accumulated is correlated to operational temperature of distillation	
Accumulated Distillate	AET	.680*	2.18E-02	9	Distillate accumulated is correlated to atmospheric equivalent temperature of distillation operation conditions	WEAKLY SIG.

** Significant at 0.01 level
* Significant at 0.05 level

The most significant correlation for GTW and SSG was the positive trend between sulfur content and TAN. Distillation temperatures also showed high correlations to TAN and sulfur content. SSG showed more significant correlations (significant below 0.01 level) but this could be due to the lower number of SSG samples compared to GTW samples.

3.4. Conclusions

The conversion of brown grease to biodiesel is a complex process but has been refined through experimentation. The esterification reactions performed in the bubble column reactors have shown effective conversion of the FFA to FAME. The washing stage has been more complicated than expected because of the formation of the emulsion layer; however this problem can be reduced by using spray washes. The emulsion layer can also be removed, heated, and recover a high-FFA content material which has potential to be recycled and esterified in a next batch of brown grease.

The distillate FAME after vacuum distillation meets all of the ASTM D6751 specifications except for TAN, oxidation stability, and sulfur content. The latter is the most difficult to resolve because there is no simple additive that can be used to meet the specification. Vacuum distillation has proven effective at reducing the sulfur content by 75-96% from brown grease to distillate FAME with a consistent distillate sulfur content of about 30 ppm S. However, reducing sulfur content in this distillate is challenging.

Correlating the temperature to sulfur content and TAN is slightly difficult because of the light and heavy distillate at the beginning and end of distillation. The Vigreaux distillation shows that throughout the distillation, there appears to be a parabolic trend for the TAN and sulfur content of the distillate biodiesel. The sulfur results of this

distillation are similar to Chakrabarti et al.; however, they did not track the distillate TAN of the collected fractions throughout distillation.

The biodiesel production process presented in this chapter has shown effectiveness at reducing the sulfur and has resulted in a patent application (Stacy et al., 2015a, 2015b) and two invention disclosures (Cairncross et al., 2016a, 2016b). This research was also included in reports for the EPA SBIR and WERF grants.

Chapter 4. Life Cycle Assessment of Biodiesel Produced from Grease Trap Waste

4.1. Introduction

Life cycle assessment (LCA) is a systematic framework for examining the implications of products, processes, and activities, using specific metrics through life cycle impact assessment that approximate environmental damages (2006). The research presented in this chapter focuses on the production of biodiesel from GTW utilizing a process model created from laboratory data from our recent reactor and purification research. The LCA included the entire life cycle of the fuel from the collection of the GTW feedstock to the combustion of the biodiesel in a vehicle. This study included a parametric study on lipid content of the GTW to analyze the 100-y global warming potential, fossil cumulative energy demand, and selected air pollution emissions associated with the combustion of the fuel.

LCA has been used to estimate the life cycle impact assessment (LCIA) metrics for biodiesel produced from a variety of feedstocks. Dufour and Iribarren performed LCA on biodiesel production from inedible and low-quality biodiesel feedstocks such as sewage sludge and used vegetable oil. They showed that the production of biodiesel from used vegetable oil and from sewage sludge reduced greenhouse gas (GHG) emissions by 79.7% and 24.5%, respectively as compared to low-sulfur diesel (Dufour & Iribarren, 2012). The sewage sludge GHG reduction is smaller because 10,000 kg of sewage sludge was needed to be processed to produce 1,000 kg of biodiesel whereas only 1205 kg of waste vegetable oils is needed for 1,000 kg of biodiesel (Dufour & Iribarren, 2012). The variability of lipid concentration in sewage sludge is similar to that of GTW;

the lower the lipid content, the greater volume of starting waste material is needed to produce the same amount of fuel. Tu and McDonnell published an analysis of the life cycle energy and greenhouse gas emissions of GTW-biodiesel processing and performed Monte Carlo simulation for a sensitivity analysis. They found that the GTW biodiesel process had potentially lower GHG emissions and energy usage than conventional fuels primarily when anaerobic digestion was used for waste disposal (Tu & McDonnell, 2015). However, this analysis relied on literature for the GTW-biodiesel production and excluded the biodiesel purification step necessary for compliance with ASTM-grade biodiesel.

GTW disposal methods vary based on location and municipal regulations (Wiltsee, 1998). Common practices are to dispose of GTW at a landfill, incinerator, or anaerobic digester (Long et al., 2012). The degradation of organic material in a landfill emits methane gas (biogas), which is a more potent greenhouse gas (GHG) than carbon dioxide (CO_2) (Sundqvist, 1999; 2012) and accounts toward GHG emissions, unlike biogenic CO_2; the collection and use of this biogas can benefit waste disposal facilities. Landfill gas collection and anaerobic digestion offer ways to reduce the GHG emissions from the methane gas by flaring or cogenerating heat and electricity; these processes convert the CH_4 to biogenic CO_2, which is considered to be a short-lived form of carbon, unlike fossil CO_2 emissions (Foster et al., 2007). Recent laboratory and LCA research has focused on anaerobic co-digestion of GTW with residual biosolids such as sewage sludge (Gough et al., 2013; Long et al., 2012; Razaviarani et al., 2013; Silvestre et al., 2011); however, extracting the brown grease lipids for biodiesel production and anaerobic digestion of the wastewater has been reported to produce more usable energy

than anaerobic digestion alone (Lopez et al., 2014). Also, the variability of the feedstock could affect the microbiological activity in the anaerobic digester, which is sensitive to changes in feedstock composition, particularly long-chain fatty acids (Lopez et al., 2014). Separating brown grease lipids from GTW for biodiesel production has several potential benefits for waste management facilities, including reducing the volume of GTW that is processed for disposal and replacing petroleum diesel combustion by a renewable fuel.

4.2. Research Scope and Methods

4.2.1. Goal and Scope

LCA was used to evaluate the energy and selected LCIA metrics of producing and combusting 1 MJ of biodiesel (the functional unit) from GTW. The LCIA metrics analyzed were midpoint life cycle impact assessment metrics of 100-y global warming potential (GWP_{100}) (Foster et al., 2007), fossil cumulative energy demand (CED_{fossil}) (Frischnect et al., 2007), and criteria air pollutant emissions (Jungbluth et al., 2007): carbon monoxide (CO), mono-nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter (PM).

LCA can be performed using an attributional or a consequential framework. Attributional LCA is used to determine the total emissions from the process (Brander et al., 2008; Rehl et al., 2012) whereas consequential LCA is used for analyzing the change in emissions which is due to a change in process for handling GTW (Brander et al., 2008; Rehl et al., 2012). In this study, an attributional LCA of the GTW biodiesel process was first used to determine the LCIA metrics of the entire biodiesel production process including the transportation of GTW from restaurants to the grease hauler's aggregation location (transfer station), separation of GTW brown grease lipids, disposal of GTW

wastewater and waste solids, conversion of brown grease lipids into fuel, and operation of fuel in a vehicle. Despite brown grease lipid separation, there is still a large volume of wastewater and solids that need to be disposed of, which leads to high greenhouse gas emissions (Tu & McDonnell, 2015); therefore, a consequential LCA was also used to examine the GWP_{100} of the GTW biodiesel process and to compare it with current disposal of the same amount of GTW (brown grease lipids not separated for biodiesel production). GTW disposal at a landfill was chosen; other waste disposal options such as incineration and anaerobic digestion are outside the scope of this study and will be addressed in Chapter 5. Lastly, the sensitivity of LCA impacts due to the variability of brown grease lipid content in the GTW was evaluated using a Monte Carlo simulation.

This study utilized various tools for the LCA to determine the LCIA metrics of the fuel processes. SimaPro8 (PRéConsultants, 2014) and the EcoInvent database (Jungbluth et al., 2007) were used to analyze the impacts for the GTW biodiesel production except for the natural gas used for steam production. GREET2014 (Argonne National Laboratory, 2014) was used to determine the life cycle impacts of natural gas used for steam production, the soybean biodiesel process, the LSD process, and vehicle operation because GREET is specific towards the production and combustion of these fuels in the United States. Oracle Crystal Ball (Oracle, 2014) was used to run a Monte Carlo simulation for the sensitivity of brown grease lipid content on the LCIA metrics.

4.2.2. System Boundary

A total of three fuel production processes and one comparative process were studied for the production of biodiesel from GTW (Figure 4.1), current GTW disposal, biodiesel from soybeans, and LSD. The system boundary of the life cycle model of the

fuel production process included three stages: (1) pretreatment, (2) fuel production, and (3) vehicle operation.

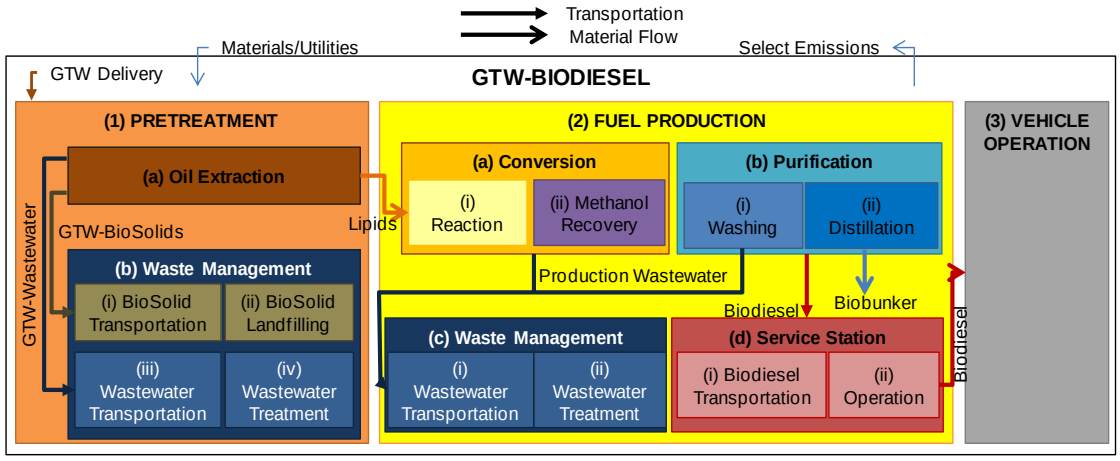


Figure 4.1: System boundary for the GTW biodiesel process. Each of the three main stages include the material and energy inputs and emission outputs for (1) pretreatment (orange), (2) fuel production (yellow), and (3) Vehicle operation (gray). Some process stages have a sub-stage marked with letters a-d and some sub-stages have individual steps marked i-iv.

4.2.3. Process Description for Biodiesel Produced from Grease Trap Waste

A process model was created using laboratory data (Mohammed, 2011; Stacy et al., 2014) and unit operation material balances from design projects (Bucher et al., 2014; Haas, Sanchez, et al., 2005; Lam et al., 2010) to estimate energy and material requirements.

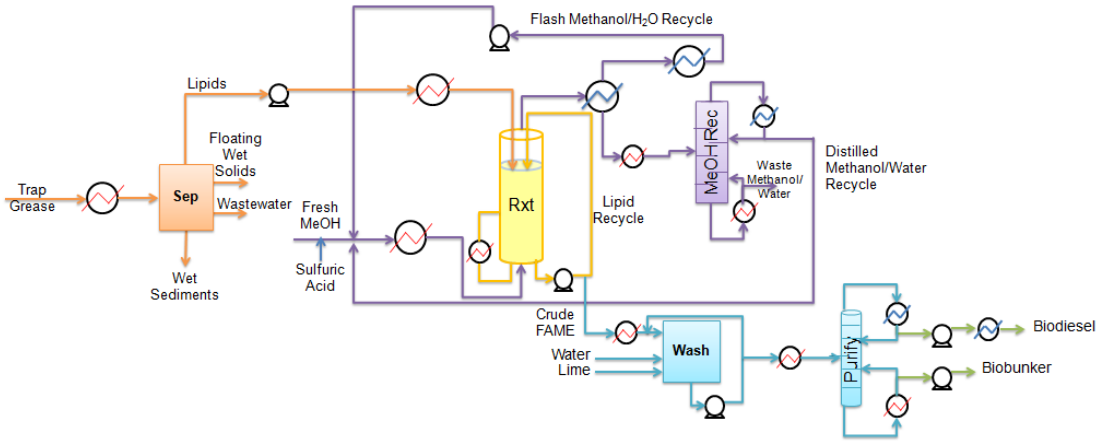


Figure 4.2: Process flow diagram for the GTW biodiesel process. Process stages are represented: pretreatment lipid separation (orange), biodiesel reaction (yellow), methanol recovery (purple), and washing/distillation (teal).

The process model (Figure 4.2) simulated a GTW biodiesel plant with a capacity for producing 840 L/day of biodiesel and analyzed the material and energy requirements for the GTW biodiesel process. The model included the extraction of grease lipids from GTW, conversion of lipids into biodiesel with methanol recycling, washing of crude biodiesel, and purification using vacuum distillation.

4.2.3.1. Transportation of Grease Trap Waste to Transfer Station

The GTW was delivered to the transfer station in a 16 metric-ton truck with a round-trip transportation distance of 286 km using data collected from routes traveled by Russell Reid Waste Management (RRWM) grease haulers during the longitudinal study. The route distances are shown in Table 4.1. The environmental impacts were determined using transportation emissions data in SimaPro8.

Table 4.1: Transportation distance of grease trap waste from interceptors to transfer station.

Sampling Date	Route, km
6/26/2014	140
7/3/2014	170
7/15/2014	192
7/25/2014	144
8/11/2014	364
12/8/2014	157
1/8/2015	272
2/3/2015	518
2/19/2015	223
3/10/2015	234
4/8/2015	407
4/17/2015	320
4/27/2015	373
5/11/2015	344
6/2/2015	459
6/23/2015	266
Average	**286**

4.2.3.2. Pretreatment

The GTW pretreatment stage included two sub stages: oil extraction (separation of brown grease lipids) and waste management (WM).

4.2.3.2.1. Oil Extraction

The oil extraction separated the lipids from the remaining GTW (floating solids, wastewater, and sediments) with heating to liquefy the lipids for faster separation. The volumetric balance of the GTW brown grease lipids was varied from 2-40%, wastewater 25-64%, and the floating solids and sediments (wet solids) were kept constant at 10% and 25%, respectively. The GTW was heated to 60 °C for three hours with a heat loss of

50%. Process steam from the combustion of natural gas was used to heat the separator and electricity was used for a pump and vibrating screen.

4.2.3.2.2. Pretreatment Waste Management

The waste management included the transportation and treatment of GTW wastewater (GTW-WW) at a wastewater treatment plant as well as the transportation and disposal of GTW waste solids (GTW-WS) at a landfill. The transportation distance of both materials was 50 km in a 16 metric-ton truck.

The GHG emissions associated with the landfill was estimated using landfill data of food waste from the EPA. Food waste data were used for the GTW-WS because the GTW comes from kitchen waste (Eleazer et al., 1997). The landfill gas emitted was analyzed using two methods: (A) flaring and (B) cogeneration for electricity and heat production. The cogeneration products were treated as avoided emissions of electricity and natural gas. A diagram of landfill gas emissions and collection is shown in Figure 4.3.

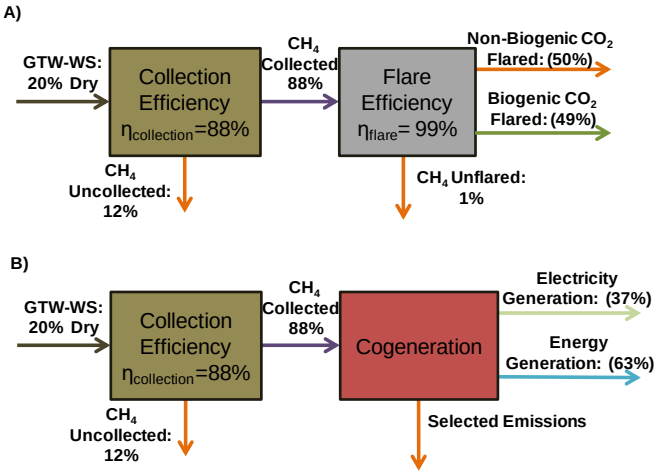


Figure 4.3: Landfill emissions mass flow diagram for treatment of landfill gas by (A) flaring and (B) cogeneration.

GTW-WS were wet when separated; a moisture content of 80% was assumed based off laboratory tests to determine the dry mass. The waste in the landfill emits CH_4 which assumed an average collection rate of 88% (USEPA, 2012). The flare landfill gas scenario included flaring with an efficiency of 99% (USEPA, 2012). Because 51% of the carbon content of food waste was biogenic (USEPA, 2012), 51% of the CO_2 that was emitted through flaring did not contribute to the GWP_{100}. The cogeneration scenario included the impacts of uncollected CH_4 and the impacts associated with the cogeneration. The cogeneration was modeled from the Ecoinvent database for bioenergy (Jungbluth et al., 2007) with an assumption of heat generation of 0.55 MJ/MJin and electricity generation of 0.32 MJ/MJin where MJin is the energy of the landfill gas that was collected. The electricity and heat produced from cogeneration were treated as avoided products where the GWP_{100} associated with electricity and the energy of natural gas for steam production were treated as a negative value.

The landfill emissions were determined by a mass balance on the degradation food waste. The total amount of CO_2 equivalents (CO_2eq) emitted to the atmosphere through flaring of landfill gas was calculated using the mass balance shown in Equation 4.1.

$$\frac{gCO_2eq}{\text{MJ}-\text{fuel}} = \{\left[300.7 * 0.2 * m_{GTW-WS,wet} * (1 - \eta_{collection})\right] + \left[300.7 * 0.2 * m_{GTW-WS,wet} * \eta_{collection} * \left(1 - \eta_{flare}\right)\right]\} * 25 * \rho_{CH_4} + \left[\left(300.7 * 0.2 m_{GTW-WS,wet} * \eta_{collection} * \eta_{flare}\right) * \rho_{CH_4}\right] * \frac{44}{16} * \%_{NonbiogenicCO_2} \quad \text{(Eq. 4.1)}$$

Where,

300.7 = CH_4 yield for food waste (ml CH_4/g dry mass)(Eleazer et al., 1997)

0.2 = dry fraction of GTW-WS (80% moisture content based on lab tests)

$m_{GTW\text{-}WS,wet}$ = GTW-WS wet mass per MJ Fuel

25 = 100-y global warming potential of CH_4 (g CO_2eq)

ρ_{CH4} = CH_4 density = 0.66 g/L

44/16 = ratio of molecular weights of CO_2/CH_4

$\%_{NonbiogenicCO2}$ = percentage of non-biogenic CO_2

η_i = efficiency at stage i: (1) CH_4 collection = 88% (USEPA, 2012) (2) CH_4 flare = 99%

The simplified GWP_{100} for the cogeneration of landfill gas was determined by using Equation 4.2.

$$\frac{gCO_2eq}{\text{MJ Fuel}} = [\text{CH}_4\text{uncollected}] + \{[\text{Cogeneration}\text{GWP}_{100} + \text{Lubricant}\text{GWP}_{100}]\} - \{[\text{Avoided}\text{GWP}_{100}]\} \quad \text{(Eq. 4.2)}$$

The GWP_{100} was determined by summing the GWP_{100} of the uncollected CH_4, the GWP_{100} for the lubricant use and disposal in cogeneration and subtracting the impacts associated with the electricity and natural gas that were avoided because of the cogeneration. The LCIA values for lubricant, cogeneration, electricity, and heat were defined by the life cycle inventory for bioenergy data as "per MJ" of CH_4 into the process (Table 4.2); therefore, these impacts were multiplied by the energy of CH_4 collected.

The GWP_{100} of the uncollected CH_4 was determined using Equation 4.3.

$$\mathrm{CH_4uncollected} = \frac{gCO_2eq}{\mathrm{MJ\ Fuel}}$$

$$= \left[300.7 * 0.2 * m_{GTW-WS,wet} * (1 - \eta_{collection})\right] * 25 * \rho_{CH_4} \text{ (Eq. 4.3)}$$

The amount of landfill gas produced were determined by truncating Equation 4.2 before the flaring emissions and converting to energy using the lower heating value of 0.0359 MJ/L.

$$\mathrm{E_{CH4}collected} = \frac{\mathrm{E_{CH4}}}{\mathrm{MJ\ Fuel}}$$

$$= \left\{\left[300.7 * 0.2 * m_{GTW-WS,wet} * (\eta_{collection})\right]\right\} * 0.0359 \quad (Eq. 4.4)$$

The GHGs associated with GWP_{100} and materials used for cogeneration were determined using Table 13.12 in the life cycle inventories of bioenergy data (Jungbluth et al., 2007) summarized in Figure 4.2 below.

Table 4.2: Summary of cogeneration inventory for 1 MJ of energy into process stage

Item	Unit	Value
Generated electricity	MJ/MJin	0.32
Generated heat	MJ/MJin	0.55
Lubricating oil	kg/MJin	3.00E-05
Disposal mineral oil	kg/MJin	3.00E-05
Methane (CH_4)	kg/MJin	2.30E-05
Nitrous oxide (N_2O)	kg/MJin	2.50E-06

The GWP_{100} for the cogeneration GHGs were determined using the Equation 4.5.

$$\mathrm{CogenerationGWP_{100}} = \frac{gCO_2eq}{\mathrm{MJ\ Fuel}}$$

$$= [\mathrm{E_{CH4}collected}] * \{[\mathrm{CH_4} * 25 + \mathrm{N_2O} * 298] * 1000\} \quad \text{(Eq. 4.5)}$$

The GWP_{100} associated with the lubricant were determined by multiplying the energy collected (Equation 4.4) by the amount of lubricating oil and GWP_{100} of lubricating oil shown in Equation 4.6.

$$\begin{aligned}\mathrm{Lubricant}GWP_{100} &= [E_{CH4}\mathrm{collected}] \\ &* \{[\mathrm{LubricatingOil} * GWP_{100}\mathrm{LubricatingOil}] \\ &+ [\mathrm{DisposalMineralOil} * GWP_{100}\mathrm{DisposalMineralOil}]\}\end{aligned} \quad \text{(Eq. 4.6)}$$

The avoided emissions were calculated using Equation 4.7:

$$\begin{aligned}\mathrm{Avoided}GWP_{100} &= [E_{CH4}\mathrm{collected}] \\ &* \{[\mathrm{GeneratedElectricity} * GWP_{100}\mathrm{Electricity}] \\ &+ [\mathrm{GeneratedHeat} * GWP_{100}\mathrm{NaturalGas}]\}\end{aligned} \quad \text{(Eq. 4.7)}$$

Equations 4.3 to 4.7 were combined and substituted into 4.2 which produced Equation 4.8 for the total GWP_{100} of landfill gas cogeneration.

$$\begin{aligned}\mathrm{Total}GWP_{100} = \frac{gCO_2eq}{\mathrm{MJ-fuel}} &= \left[300.7 * 0.2 * m_{GTW-WS,wet} * (1 - \eta_{collection})\right] * 25 * \rho_{CH_4} + \\ &\left\{\left[300.7 * 0.2 * m_{GTW-WS,wet} * (\eta_{collection})\right]\right\} * 0.0359 * (\{[CH_4 * 25 + N_2O * 298] * \\ &1000\} + \{[\mathrm{LubricatingOil} * GWP_{100}\mathrm{LubricatingOil}] + [\mathrm{DisposalMineralOil} * \\ &GWP_{100}\mathrm{DisposalMineralOil}]\} - \{[\mathrm{GeneratedElectricity} * GWP_{100}\mathrm{Electricity}] + \\ &[\mathrm{GeneratedHeat} * GWP_{100}\mathrm{NaturalGas}]\})\end{aligned} \quad \text{(Eq. 4.8)}$$

4.2.3.3. Fuel Production

The fuel production stage contained four sub-stages: conversion, purification, waste management, and service station. A co-product biobunker was produced which is similar to a heavy fuel oil.

4.2.3.3.1. Conversion

The brown grease lipids were reacted using a bubble column reactor that was developed by researchers at Drexel University (Stacy et al., 2014) and was inspired by experiments done by Kocsisová et al. *(Kocsisova et al., 2005)*. The brown grease lipids contained 97% free fatty acids which was the typical content found at the time the process model was created. Oleic acid was used to represent the free fatty acids because it is the most prevalent fatty acid in waste oils (Canakci & Van Gerpen, 2001; Long et al., 2012). Transesterification was not included due to the high level of free fatty acids. The esterification was performed at atmospheric pressure and 120 °C for 2 h utilizing 0.5% w/w sulfuric acid as catalyst and 4.5 molar ratio of methanol to lipids.

Methanol was recovered and recycled to the reactor using a partial condenser and a distillation column. The distillation column had a reflux ration of 1.5 and a reboil ratio of 2 assuming pure methanol and water, respectively. A fractional recovery of water in the distillate was estimated to be 16.1%. Methanol was recovered 85% by mole in distillate during fractional distillation and 99% of methanol was recovered in the distillate of the distillation column. Natural gas combusted for process steam, cooling water, and electricity were used for heating/cooling and for powering pumps.

4.2.3.3.2. Purification

The crude biodiesel was first neutralized and water washed and then distilled in a short-path evaporator for further purification and sulfur reduction. GTW biodiesel had a high sulfur concentration because the sulfur content of GTW brown grease lipids was about 200 ppm S on average (shown in Chapter 3.3.3.1). Vacuum distillation was necessary to reduce the sulfur concentration (Gardner et al., 2013) to meet the 15 PPM

sulfur specifications for on-road biodiesel (ASTM, 2015). The evaporator was operated at 0.1 bar and 260 °C. This condition is conservative compared to more recent experimental data (performed in Chapter 3) operating at 1 mbar and 190 °C with optimization ongoing. Therefore, the energy demand for the evaporator in this study was likely higher than necessary. This stage was essential for sulfur reduction and was not considered by Tu and McDonnell (Tu & McDonnell, 2015).

The high-boiling point material remaining after distillation was described as biobunker. Because allocation methods could change the life cycle impact of a process and the mass/volume/energy of biobunker compared to biodiesel was small, no allocation method was applied to this LCA. Thus, the GTW biodiesel LCIA metrics estimated in this analysis are conservative. Potentially, future work could assign an allocation to the biobunker or it could be evaluated as a substitute for industrial use of natural gas for steam production or of heavy fuel oil.

4.2.3.3.3. Fuel Conversion Waste Management

The wastewater produced from the methanol recovery and water washing was transported 50 km by a 7.5 metric-ton truck for treatment at a wastewater treatment plant.

4.2.3.3.4. Service Station

The purified biodiesel was transported 100 km by a 7.5 metric-ton truck to the service station. Service station operations were evaluated according to SimaPro8 (PRéConsultants, 2014).

4.2.3.4. Vehicle Operation

The use and end-of-life of biodiesel was combustion in a vehicle. The CO_2 credit for biodiesel was represented in the fuel's combustion. The CO_2 produced from biogenic

sources was considered zero because of the recent sequestration of carbon from the atmosphere as opposed to that of petroleum fuels (Goedkoop et al., 2008). Biodiesel from oleic acid was treated as methyl oleate, which consists of 19 carbons: 18 renewable, biogenic carbon atoms from the lipids and one non-renewable, non-biogenic carbon from the methanol. Therefore, the biodiesel combustion emissions from non-renewable sources were $1/19^{th}$ of the total CO_2 combustion emissions.

The vehicle operation of the GTW and soybean biodiesel were evaluated in the same way using GREET2014 (Argonne National Laboratory, 2014) vehicle combustion data combined with biodiesel emission data reported in a review by the U.S. Environmental Protection Agency (USEPA). The USEPA performed a study and fit an emissions curve to data from a compilation of literature reports on the engine combustion of biodiesel for CO, NO_x, and PM which was then represented as a percent change from LSD (USEPA, 2002). The sulfur content of the fuel was used to determine SO_x emissions. This study assumed sulfur content of 15 ppm for GTW biodiesel despite the ongoing optimization of vacuum distillation.

4.2.4. Comparative Scenarios

The current GTW disposal represented the transportation of GTW to the transfer station, gravity settling of the GTW where GTW-WS and brown grease lipids were dewatered and sent to the landfill while the GTW-WW was sent to wastewater treatment. The LCIA metrics associated with the transportation, wastewater treatment, and landfill were treated the similarly to the GTW biodiesel process description. It was assumed that the emissions associated with the GTW gravity settling were negligible.

Soybean biodiesel and LSD life cycle assessments were reported using the GREET2014 fuel processes. Details on these processes can be found Appendix C.2.1.

4.2.5. Life Cycle Inventory (LCI)

The materials and energy required for the biodiesel production are shown in Table 4.3 designated by the LCIA database and program that was used to determine the environmental impacts of the specific item.

Table 4.3: Life cycle inventory by component and database.

	Name in Database	Database	Program
INPUTS			
Materials			
Sulfuric acid	Sulphuric acid, liquid, at plant/RER U	Ecoinvent	SimaPro8
Methanol	Methanol, at regional storage/CH U	Ecoinvent	SimaPro8
Wash water	Water, deionised, at plant/CH U	Ecoinvent	SimaPro8
Sodium hydroxide	Sodium hydroxide, production mix, at plant/kg/RNA	USLCI	SimaPro8
Utilities			
Natural gas for steam production			GREET2014
Electricity	Electricity, medium voltage, at grid/US U	Ecoinvent	SimaPro8
Cooling water	Water, decarbonised, at plant/RER U	Ecoinvent	SimaPro8
OUTPUTS			
Materials			
Production wastewater	Waste water – untreated, slightly organic contaminated EU-27 S	ELCD	SimaPro8
GTW wastewater	Waste water – untreated, EU-27 S	ELCD	SimaPro8
GTW waste solids: methane gas production	Food Waste	Landfill Literature	Calculation
GTW waste solids: cogeneration		EcoInvent	Calculation
Transportation			
Biodiesel	Transport, lorry >16t, fleet average/RER U	EcoInvent	SimaPro8
Production wastewater	Transport, lorry >16t, fleet average/RER U	EcoInvent	SimaPro8
GTW wastewater	Transport, lorry >16t, fleet average/RER U	EcoInvent	SimaPro8
GTW waste solids	Transport, lorry >16t, fleet average/RER U	EcoInvent	SimaPro8

A process-based LCI model was developed from sequential material and energy balances following international organization and standardization (ISO) methods (2006).

Data were used to create an inventory of the materials and utilities required for producing 1 MJ of biodiesel (MJ Fuel) from GTW, shown in the following tables.

Table 4.4: Life cycle inventory inputs for GTW biodiesel production with lipid contents of 2-40%.

	Lipid Content	2%	3%	4%	5%	7%	10%	20%	30%	40%
	INPUTS/MJ biodiesel									
	Materials									
1	Sulfuric acid, kg [a]	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
2	Methanol, kg [a]	0.0029	0.0029	0.0029	0.0029	0.0029	0.0029	0.0029	0.0029	0.0029
3	Wash water, kg [a]	0.0295	0.0295	0.0295	0.0295	0.0295	0.0295	0.0295	0.0295	0.0295
4	Sodium hydroxide, kg [a]	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
	Utilities									
	Oil Extraction									
5	Natural gas for steam production, m^3 [b]	0.0115	0.0076	0.0057	0.0045	0.0032	0.0022	0.0011	0.0007	0.0005
6	Electricity, kWh [a]	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
	Conversion									
7	Natural gas for steam production, m^3 [b]	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020	0.0020
8	Electricity, kWh [a]	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
9	Cooling water, kg [a]	0.7255	0.7255	0.7255	0.7255	0.7255	0.7255	0.7255	0.7255	0.7255
	Purification									
10	Natural gas for steam production, m^3 [b]	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017
11	Electricity, kWh [a]	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
12	Cooling water, kg [a]	0.9982	0.9982	0.9982	0.9982	0.9982	0.9982	0.9982	0.9982	0.9982

[a] SimaPro8 (PRéConsultants, 2014)
[b] GREET2014 (Xie et al., 2011)
[c] Landfill Literature (Eleazer et al., 1997; USEPA, 2012)/EcoInvent database (Jungbluth et al., 2007)

Table 4.5: Life cycle inventory outputs for GTW biodiesel production with lipid contents of 2-40%.

	Lipid Content	2%	3%	4%	5%	7%	10%	20%	30%	40%
	OUTPUTS/ MJ Biodiesel Materials									
13	GTW biodiesel, kg	0.0265	0.0265	0.0265	0.0265	0.0265	0.0265	0.0265	0.0265	0.0265
14	Biobunker, kg	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
15	GTW wastewater, kg [a]	0.9084	0.5960	0.4398	0.3460	0.2389	0.1586	0.0649	0.0336	0.0180
16	Production wastewater, kg [a]	0.0323	0.0323	0.0323	0.0323	0.0323	0.0323	0.0323	0.0323	0.0323
17	GTW waste solids, kg [c]	0.5046	0.3364	0.2523	0.2019	0.1442	0.1009	0.0505	0.0336	0.0252
	Transport									
18	Biodiesel, tkm* [a]	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026
19	GTW wastewater, tkm* [a]	0.0454	0.0298	0.0220	0.0173	0.0119	0.0079	0.0032	0.0017	0.0009
20	Production wastewater, tkm* [a]	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
21	GTW waste solids, tkm* [a]	0.0252	0.0168	0.0126	0.0101	0.0072	0.0050	0.0025	0.0017	0.0013

*metric ton times kilometers traveled
[a] SimaPro8 (PRéConsultants, 2014)
[b] GREET2014 (Xie et al., 2011)
[c] Landfill Literature (Eleazer et al., 1997; USEPA, 2012)/EcoInvent database (Jungbluth et al., 2007)

The full inventory for 2-40% brown grease lipid content is shown for inputs in Table 4.4 and outputs in Table 4.5. Most of the materials and utilities were independent of brown grease lipid content with the exception of rows 5, 15, 17, 19, 21 which were part of the pretreatment process. To produce 1 MJ of biodiesel, the amount of GTW entering the process needed to increase as brown grease lipid content decreased; unlike the constant GTW input studied by Tu and McDonnell where biodiesel production was varied. In this scenario, many of the inputs did not change with brown grease lipid content because they were proportional to the amount of biodiesel produced. When brown grease lipid content decreased, the pretreatment required more energy and

produced more GTW-WW and GTW-WS that needed to be transported and treated for disposal.

4.2.6. Uncertainty/Model Fitting

A model was developed to analyze and test trends in the LCIA metrics of producing biodiesel from GTW with varying brown grease lipid contents shown in Equation 4.9.

$$\frac{I_{Total}}{E_{Biodiesel}} = \frac{\dot{M}_{GTW}\hat{I}_{PT} + \dot{M}_{Lipids}\hat{I}_{FP} + \dot{M}_{Biodiesel}\hat{I}_{VO}}{\dot{M}_{Biodiesel}\Delta\hat{H}_c} \quad \text{(Eq. 4.9)}$$

Where,

$\hat{I}_i$ = environmental impact intensity of process stage i per unit mass of input (PT = pretreatment, FP = fuel production, and VO = vehicle operation: combustion emissions)

$\dot{M}_j$ = mass flowrate of j entering into the process stage

$\Delta\hat{H}_C$ = heat of combustion of biodiesel (lower heating value)

$E_{Biodiesel}$ = energy content of biodiesel produced

The impact intensity factors $\hat{I}_i$ approximated the environmental impacts per unit of feedstock entering each stage (GTW entered the pretreatment stage, GTW brown grease lipids entered fuel production stage, and biodiesel entered the vehicle operation stage). The relationship between the feedstock flow rates (Equation 4.10 was estimated using the brown grease lipid content of GTW as x and the yield of the fuel production process as ϕ:

$$\dot{M}_{Biodiesel} = \phi\dot{M}_{Lipids} = \phi x\dot{M}_{GTW} \quad (Eq. 4.10)$$

Equations 4.9 and 4.10 were combined to produce a relationship between the total impacts and GTW brown grease lipid content that was useful for analyzing the LCA results shown in Equation 4.11.

$$\frac{I_{Total}}{E_{Biodiesel}} = \left(\frac{\hat{I}_{PT}}{\phi \Delta \widehat{H}_c}\right)\frac{1}{x} + \left(\frac{\hat{I}_{FP}}{\phi \Delta \widehat{H}_c} + \frac{\hat{I}_{VO}}{\Delta \widehat{H}_c}\right) \qquad (Eq. 4.11)$$

Equation 4.1 predicts that the total environmental impacts are proportional to the reciprocal of the GTW brown grease lipid content, *1/x*. The reciprocal of the brown grease lipid content is a measure of the amount of GTW that must be processed to produce a given amount of biodiesel. In the LCA model, more brown grease lipid contents were used in the low-range lipid contents (2%, 3%, 4%, and 5%) to best represent the hyperbolic rise. Linear regression of Equation 4.11 to the theoretical environmental impacts versus *1/x* was used to estimate slope and intercept. For the model fitting, the lipid content by volume was inverted to produce 1/*x*. Multiplying by the density of the GTW (1.1 kg/L) gave the lipid content by percent mass.

This equation predicted that the total LCIA metrics were linearly proportional to the reciprocal of the GTW lipid content, *1/x*. Linear regression of Equation 4.11 to the LCA results for LCIA metrics versus *1/x* was used to estimate the slope and intercept.

4.2.7. Sensitivity to Grease Trap Waste Composition and Monte Carlo Simulation

Monte Carlo simulation was used to test the effects of lipid variability on GWP_{100} and other LCIA metric metrics. A distribution curve was fit to lipid percentages that were found during a longitudinal study of GTW composition (Cairncross et al., 2015). LCIA metrics were found by utilizing the fitted equation described in the previous section where lipid content, *x*, was varied using the distribution curve. Oracle Crystal Ball was used to determine the distribution curve of the lipids running Monte Carlo in 5,000 trials.

The GTW biodiesel process was also sensitive to the FFA content of the GTW lipids. The process model assumed a 97% FFA content representative of laboratory data

collected at the time of its development. A scenario of using a lower FFA content was examined and is discussed in Appendix C.3.1. Tu and McDonnell also performed a sensitivity analysis on brown grease lipid content, FFA content, and other anaerobic digestion conditions (Tu & McDonnell, 2015). They found the greatest variability for GHG emissions was due to changes in brown grease lipid concentration; therefore, the Monte Carlo analysis in this chapter was only applied to brown grease lipid content sensitivity.

4.3. Results and Discussion

The parametric life cycle results represented the LCIA metrics for 1 MJ of biodiesel produced from GTW with a lipid content of 2-40%. The GWP_{100}, CED_{Fossil}, and selected air emissions for the GTW biodiesel process were studied and compared to soybean biodiesel and LSD (shown in detail in Appendix C.2.1).

4.3.1. 100-Year Global Warming Potential

4.3.1.1. Attributional Life Cycle Assessment Approach for Biodiesel Produced from Grease Trap Waste

The life cycle GWP_{100} of GTW biodiesel by process stage, with brown grease lipid content ranging from 2-40% was evaluated in two scenarios for treatment of the landfill gases from disposal of the GTW-WS: flaring (Figure 4.4-A) and cogeneration of heat and electricity (Figure 4.4-B). The impact due to the waste management of the pretreatment is presented separately from the rest of the pretreatment (steam production and electricity) because of its large contribution to the emissions. For brown grease lipid contents less than 10%, the GWP_{100} of the process was dominated by the emissions from

delivery of the GTW to the transfer station and the pretreatment waste management (pretreatment WM; the transportation and treatment of GTW-WW and GTW-WS).

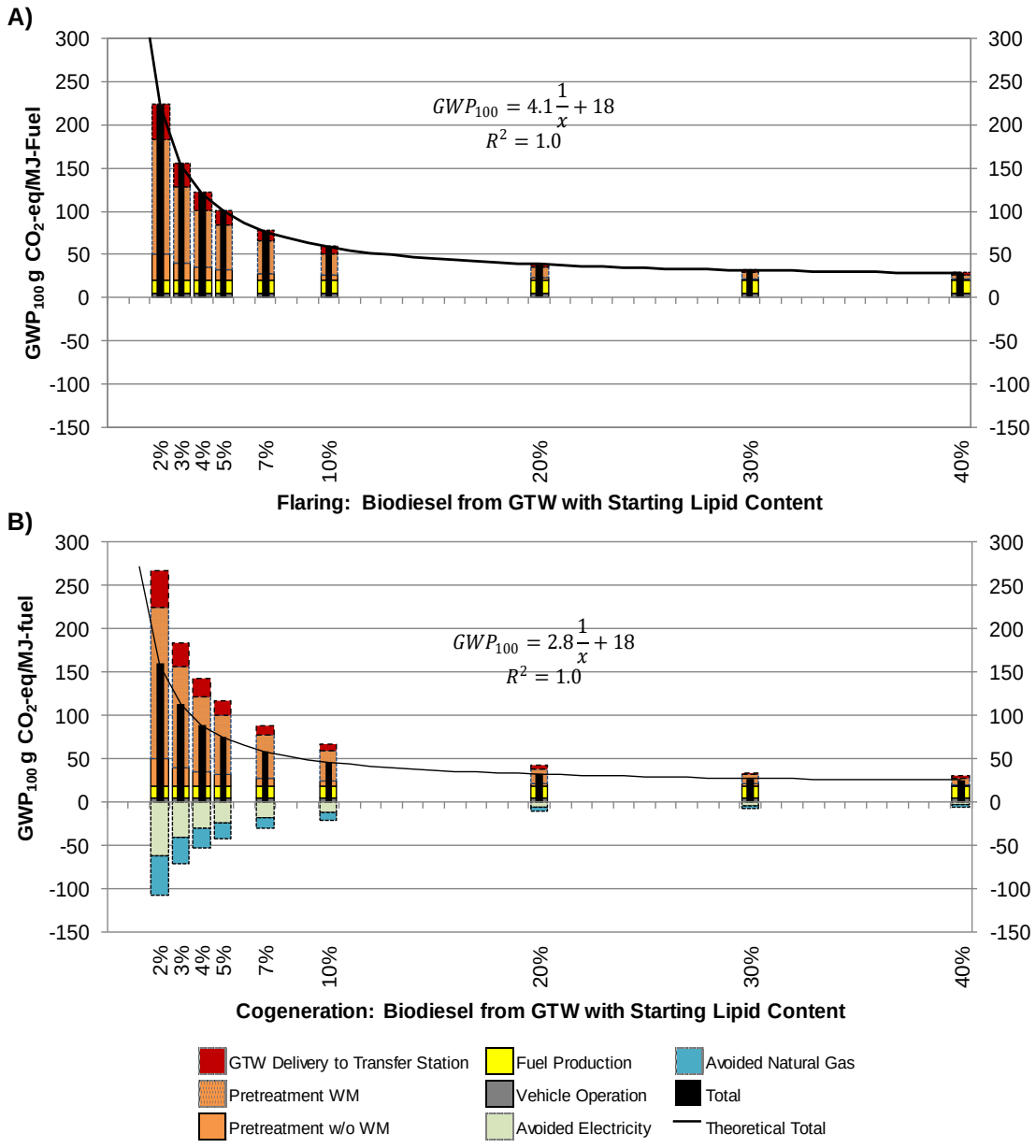


Figure 4.4: Attributional LCA approach for the parametric study on the affect of lipid content on the total GWP_{100} for GTW biodiesel process: (A) flared landfill gas and (B) cogeneration of landfill Gas. The stacked bars represent GTW biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total GWP_{100} and modeled curve (black line) are also shown.

As brown grease lipid content decreased, there was an increased amount of GTW transported to the transfer station and an increased amount of waste sent for disposal which contributed to the higher GWP_{100}. The impact from the pretreatment without WM and the fuel process stages were all dominated by combustion of natural gas for steam production; as the brown grease lipid content increased, there was less natural gas consumed to produce steam to separate the brown grease lipids, which lead to a lower GWP_{100}.

The difference in the total GWP_{100} between the flaring and cogeneration scenarios was small at higher brown grease lipid contents. The flaring scenario had 11% higher total GWP_{100} compared to cogeneration (difference of 3 g CO_2eq/MJ Fuel) at 40% lipid contents. At 2% lipid content, the flaring scenario has 28% higher total GWP_{100} (difference of 64 g CO_2eq/MJ Fuel). The benefits of cogeneration were the avoided GWP_{100} from the electricity and natural gas (shown as a credit or a negative contribution to GWP_{100} in Figure 2B) which caused lower GWP_{100} for the cogeneration scenario.

The curves in Figure 4.4 are a correlation based on a linear regression of Equation 4.11 to the GWP_{100} results (equation shown in each graph). In the correlation, the constant (~18 g CO_2eq/MJ Fuel) represents the GWP_{100} of the fuel production and vehicle operation which is independent of brown grease lipid content because the feedstock volume is adjusted to have the lipid volume needed to produce 1 MJ of biodiesel. When the brown grease lipid content was below 5.5% and 3.7% in the flaring and cogeneration scenarios, respectively, the net GWP_{100} for GTW was higher than that for LSD (93 g CO_2eq/MJ Fuel). The flaring and cogeneration scenarios results showed

that for brown grease lipid contents above 6%, without accounting for any offsets, the net GWP_{100} of the proposed GTW biodiesel process were lower than the LSD.

4.3.1.2. Consequential Life Cycle Assessment Approach for Grease Trap Waste Biodiesel Process versus Current Grease Trap Waste Disposal

During the accounting for the avoided emissions for replacing current GTW disposal with the proposed GTW biodiesel, the consequence or change lead to reduced LCIA metrics for all lipid contents of GTW studied. In Figure 4.5, the GWP_{100} associated with current GTW disposal and offset LSD consumption were treated as avoided emissions. The avoided emissions were treated as a credit because both offset LSD and current GTW disposal were not needed when GTW biodiesel production was implemented. In Figure 4.5-B, the cogenerated heat and electricity associated with biodiesel production (teal) was treated as a credit; however, the cogenerated heat and electricity associated with the current GTW disposal (teal stripes) was treated as a penalty. In the current GTW disposal, the avoided emissions were originally treated as a credit, but when the current GTW disposal was treated as an avoided process, the negative value associated with the credited utility was nullified. The difference between the cogenerated avoided utility emissions in the current GTW disposal and GTW-biodiesel process avoided utilities was the impacts associated with the brown grease lipids (5.5 g CO_2eq/MJ Fuel avoided utility). Tables for the current GTW disposal and the biodiesel production can be found in Appendix C.1.

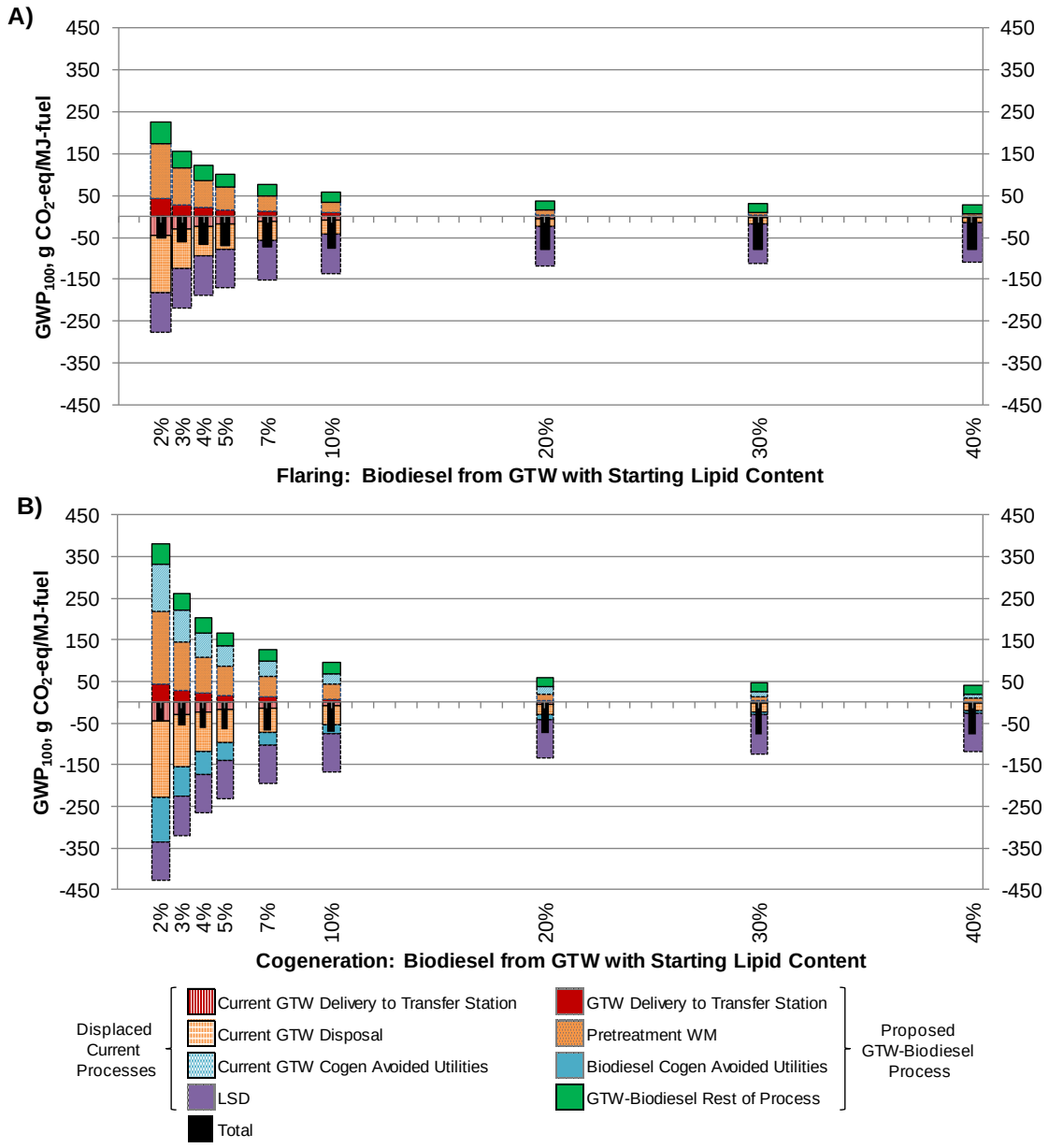


Figure 4.5: Consequential LCA approach to compare GTW biodiesel production to current GTW disposal. GWP_{100} shown for GTW -biodiesel process for (A) flared landfill gas and (B) cogeneration of landfill gas and current GTW disposal. The lipid content of the GTW was varied from 2-40%. The colored negative bars represent avoided impacts including current GTW transportation (red striped), current GTW disposal (orange hashed) and avoided impacts due to cogeneration (electricity and natural gas, blue striped) and LSD (purple). The positive bars represent the GTW transportation (red), GTW-biodiesel process (green) and the no longer avoided impacts (electricity and natural gas) from the current GTW disposal (teal). The total emissions (black bar) represent the difference between total biodiesel process and avoided emissions.

In both waste solid treatment scenarios, the total GWP_{100} associated with the GTW biodiesel process was always higher than the current GTW disposal because of additional GWP_{100} associated with the biodiesel conversion and purification processes. However, the net GWP_{100} was negative for both scenarios and all lipid contents when accounting for avoided emissions of LSD and current GTW disposal. In Figure 4.5, at low brown grease lipid contents, the largest impacts were due to waste management: positive contribution of pretreatment waste management in the GTW biodiesel process (orange with blue dots) and negative contribution of avoided waste management of the current GTW disposal (orange hashed). The difference in impacts between current GTW disposal (avoided) and pretreatment waste management was due to the brown grease lipids that were removed from GTW during pretreatment and was independent of lipid content for the chosen functional unit (1 MJ biodiesel corresponds to a constant amount of brown grease lipids). The GWP_{100} difference between the current GTW disposal and the waste disposal from biodiesel production was 7.7 and 4.5 g CO_2eq/MJ Fuel for flaring and cogeneration, respectively. The cogeneration had a smaller difference because of the reduction in avoided electricity and heat when the brown grease lipids were removed from the waste treatment (-5.5 g CO_2eq/MJ Fuel).

The removal of the brown grease lipids and production of biodiesel resulted in avoiding LSD (93 g CO_2eq/MJ Fuel). In the attributional LCA analysis of Figure 4.4, the GWP_{100} for the GTW-biodiesel process was lower than GWP_{100} of LSD for brown grease lipid contents above 5%. However in the consequential analysis of Figure 4.5, which represented replacing current GTW disposal and LSD use with the GTW biodiesel process, the net emissions (black bar) were negative for all lipid contents studied.

The GTW-biodiesel process had a better net GWP_{100} making fuel production more favorable than current GTW disposal. A new system boundary is proposed to omit the impacts associated with the current GTW disposal. For the remaining LCIA metrics we include the "without waste management" scenario (w/o WM) where the pretreatment WM and the transportation of GTW to the transfer station were omitted in the LCA of the GTW biodiesel process because these processes are already occurring.

4.3.2. Sensitivity to GTW Composition and Monte Carlo Simulation

The yield of biodiesel produced from GTW was sensitive to the composition of GTW: both the brown grease lipid content of GTW and the percent FFA of the brown grease lipids extracted from GTW. The variability of percent FFA in brown grease lipids extracted from GTW was relatively small (70% to 95%) compared to the variability in brown grease lipid content (0.15-65%); so the variability in percent FFA had a smaller effect on the LCA impacts (Tu & McDonnell, 2015). The Appendix C.3.1 includes a table that shows the sensitivity of LCA impacts to FFA content. Decreasing FFA from 97% to 80% caused a 10%-20% increase in GWP_{100} for the consequential LCA depending upon the brown grease lipid content. Chapter 5 includes sensitivity analysis for FFA content using results from the longitudinal study presented in Chapter 2 and incorporates a two-step biodiesel conversion process for both FFA and acyl glycerides present in the brown grease lipids.

The Monte Carlo analysis results presented in Figure 4.6 correspond to three scenarios: (1) attributional LCA with landfill gas flaring, (2) attributional LCA with landfill gas cogeneration, and (3) LCA omitting impacts that were from GTW waste management (impacts associated with GTW transportation to the transfer station and

waste solid and wastewater disposal). To evaluate the sensitivity that brown grease lipid content had on the LCIA metrics, a Monte Carlo simulation was performed using two experimental lognormal distributions of brown grease lipid contents for GTW: the results in Figure 4.6-A and Figure 4.6-B correspond to a lipid content distribution for raw GTW (named Raw GTW) with median and mean lipid contents of 2% and 5%, respectively and the results in Figure 4C and 4D correspond to a lipid content distribution for partially-dewatered GTW (named Dewatered GTW) with median and mean lipid contents of 27% and 29%, respectively (Cairncross et al., 2015). Both lipid distributions were truncated between 0.15%-65%. Box plots of the normalized results are shown in Figure 4.6; each LCIA metric was normalized by dividing the impact by that of LSD. In Figure 4.6, the LCIA metric of LSD equals one (red lines), and the green lines represent the impacts of normalized soybean biodiesel. The lipid content distribution functions and a table of the statistical results (mean, median, standard deviation, 10 and 90 percentiles, etc. are shown in Appendix C.3).

For all but one of the LCIA metrics in Figure 4.6, the flaring scenario had the highest median value and largest range, and the without waste management scenario had the lowest median value and smallest range. The magnitudes of the LCIA metrics for the raw GTW distribution (Figure 4.6-A and Figure 4.6-B) were significantly larger than those of the dewatered GTW distribution (Figure 4.6-C and Figure 4.6-D) because raw GTW has a much larger volume and produced more wastes that were landfilled than dewatered GTW. Compared to flaring, the cogeneration scenario had 1% reduction in the median for CO, 25% for GWP_{100}, 25% for NO_x, 42% for CED_{Fossil}, and 66% for PM.

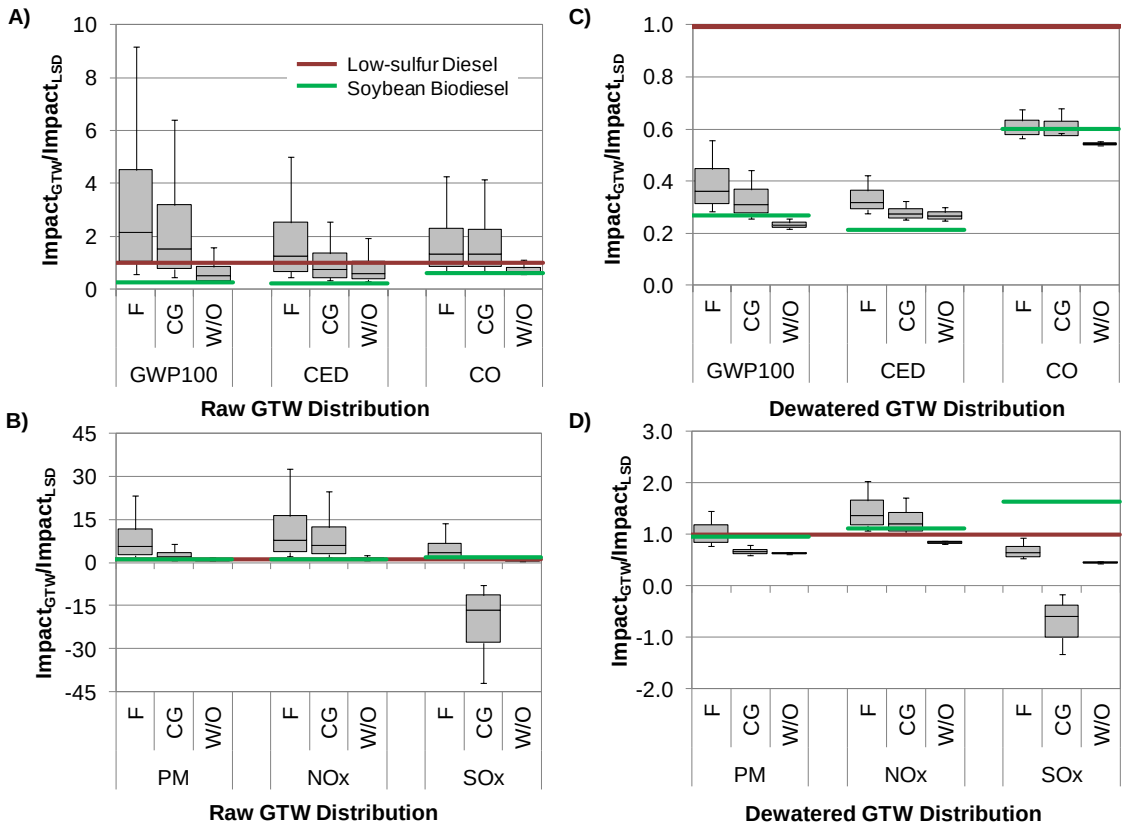


Figure 4.6: Monte Carlo analysis of the sensitivity of six LCIA metrics for several GTW waste management scenarios and two distributions of lipid content. All impacts are normalized to the corresponding impact for low sulfur diesel (LSD). Panels A and C display 100-year Global Warming Potential (GWP_{100}), Fossil Cumulative Energy Demand (CED), and carbon monoxide (CO) and panels B and D display Particulate Matter (PM), mono-nitrogen oxides (NO_x), and sulfur oxides (SO_x) emissions. Panels A and B display results based on lipid content distributions in raw GTW and panels C and D display results for dewatered GTW. Scenarios compared were landfill gas flare (F), landfill gas cogeneration (CG) and without waste management (W/O). The line in the middle of each box represents the median, the upper half of the box represents the 3rd quartile, and the lower half of the box represents the 2nd quartile. The positive and negative error bars represent the 90% and 10% percentile intervals. The green line represents soybean-biodiesel and red line represents LSD.

The SO_x emissions in Figure 4.6 were negative for the landfilling with cogeneration scenario, due to offset electricity from cogeneration, and raw GTW had more negative SO_x emissions than dewatered GTW. Also, the soybean biodiesel SO_x

emissions were higher than LSD due to sulfuric acid used in the production of phosphorous fertilizer. In this analysis the electricity was generated primarily from coal (46%) and other fossil sources (18%) which contributed to high SO_x emissions. GTW with a lower lipid content produced a higher volume of waste solids that were sent to the landfill, degraded to CH_4, generated electricity that offset grid demand and reduced SO_x emissions. This is a case of a co-product (electricity) producing a benefit in one LCIA metric that favors the co-product over the product. A similar model sensitivity was observed for ethanol produced from corn stover, where the authors found improved LCIA results at lower ethanol yields (Spatari & MacLean, 2010). However, as noted by the authors, an ethanol biorefinery would never operate at a lower yield in order to optimize offsets from its co-products (Spatari & MacLean, 2010). Similarly, a GTW biodiesel conversion process would be optimized for higher biodiesel yield for economic benefits.

Adding a dewatering step dramatically reduced the LCIA metrics because the higher brown grease lipid content of dewatered GTW (shown in Figure 4.6-C and Figure 4.6-D) required less pretreatment process energy and contained a lower volume of solid wastes for disposal. For flaring scenarios, dewatering reduced the median value of the LCIA metrics by about 80%. In cogeneration, the median values of all LCIA metrics (with the exception of SO_x) were reduced 55-80% between raw GTW and dewatered GTW. Alternatively, SO_x showed a slight increase because with the increase in brown grease lipid content in the dewatered GTW distribution, there was less solid waste sent to the landfill resulting in lower electricity credits than in the raw GTW scenario. In general, the environmental burden of producing GTW biodiesel was highly dependent on the lipid content of the GTW; if the brown grease lipid content was below 10%, LCIA

metrics increased hyperbolically (specifically shown for GWP_{100} in Figure 4.4). This result suggests that a grease dewatering process should be employed to concentrate the lipids prior to heating.

4.3.3. LCA Comparison of Biodiesel Produced from Grease Trap Waste and Inedible Feedstocks

The LCIA metrics for the GTW-biodiesel process without GTW waste management were similar to that of soybean biodiesel. In the all disposal scenarios with dewatered GTW, the GWP_{100} and CED_{Fossil} results for GTW-biodiesel were also comparable to published LCA results on biodiesel produced from other waste materials and inedible feedstocks such as jatropha. In this study, the average GWP_{100} of biodiesel produced from dewatered GTW for flare, cogeneration, and w/o WM scenarios were 37, 31, and 22 g CO_2eq/MJ Fuel. Published GWP_{100} for waste cooking oil, sewage sludge, and jatropha biodiesels were approximately 18, 20 and 35 g CO_2eq/MJ Fuel (Dufour & Iribarren, 2012; Kumar et al., 2012). In this study, the average CED_{Fossil} for the GTW flare, cogeneration, and w/o WM scenarios were 0.41, 0.34, and 0.33 MJ/MJ Fuel. Published CED_{Fossil} for waste cooking oil, sewage sludge, and jatropha biodiesels were approximately 0.2, 0.8, and 0.6 MJ/MJ Fuel, respectively (Dufour & Iribarren, 2012; Kumar et al., 2012). The GWP_{100} and CED_{Fossil} for biodiesel produced from GTW were determined by Tu and McDonnell. Scenarios with and without anaerobic digestion were evaluated and the GWP_{100} was approximately 12 and 40 g CO_2eq/MJ Fuel, respectively and the CED_{Fossil} was approximately 0.3 and 0.6 MJ/MJ Fuel, respectively (Tu & McDonnell, 2015). Table 4.6 displays the GWP_{100} and CED_{Fossil} for all waste scenarios analyzed by Tu and McDonnel and this study.

Table 4.6: Comparison of LCA results for biodiesel produced from GTW.

		GWP_{100} gCO_2eq/MJ Fuel			CED_{Fossil} MJ/MJ Fuel		
Author	**Waste Scenario**	avg	5%	95%	avg	5%	95%
Tu/McDonnell	w/Anaerobic Digestion	12	12	20	0.34	0.30	4.39
Tu/McDonnell	w/o Anaerobic Digestion	40	20	987	0.60	0.36	13.58
Hums et al.	Raw GTW: Landfill Flare	352	42	1255	2.59	0.44	8.85
Hums et al.	Raw GTW: Landfill Cogen	250	34	877	1.41	0.36	4.46
Hums et al.	Raw GTW: No Waste Treatment	37	26	59	1.10	0.34	3.30
Hums et al.	Dewatered GTW: Landfill Flare	37	26	59	0.41	0.33	0.56
Hums et al.	Dewatered GTW: Landfill Cogen	31	23	47	0.34	0.30	0.42
Hums et al.	Dewatered GTW: No Waste Treatment	22	20	25	0.33	0.30	0.38

The GWP_{100} and CED_{Fossil} data for the comparison below was estimated from Figure 6 and Figure 7 in the Tu and McDonnell paper (Tu & McDonnell, 2015). The lower heating value of 125.2 MJ/gal (Argonne National Laboratory, 2014) was used to convert the Tu and McDonnell data to a MJ of fuel basis. The system boundaries between the analyses were similar; however, this work (Hums et al.) contained the combustion of the fuel in a vehicle. The Tu and McDonnell "without anaerobic digestion" scenario included the transportation of waste solids to a landfill; however this analysis did not include the landfill gas emissions.

4.4. Conclusions

There is a trade-off between using vegetable oil such as soybean oil versus GTW brown grease lipids as feedstocks for biodiesel production. For vegetable oils, the LCIA

metrics are largely due to the pretreatment (e.g. soybean grain to soybean oil) but the conversion of vegetable oils to biodiesel is a low energy, low material process. Alternatively, the LCIA metrics from the GTW biodiesel process are primarily due to the fuel production because of the high energy required for reaction and purification into ASTM-grade biodiesel or the waste treatment (depending on the system boundary).

Because GTW-biodiesel is produced from a waste source, it is important that GTW biodiesel not only have environmental impacts comparable to or better than soybean biodiesel and LSD, but it should also be a better alternative to current GTW disposal techniques. The consequential LCA boundary demonstrated that while producing GTW biodiesel increased GHG emissions in the waste management system by 13-43 g CO_2eq/MJ Fuel, it reduced GHG emissions by 20-75% (Figure 4.5) when displacing LSD in the fully expanded system with either flaring or cogenerating electricity and heat for every MJ of biodiesel produced.

The results of this work were published in Environmental Science and Technology (Hums, Cairncross, et al., 2016).

Chapter 5. Economic and Environmental Feasibility of Producing Biofuel from Wastewater Greases

5.1. Introduction

The results in Chapter 4 showed that the environmental impacts were sensitive to lipid content and were dominated by the waste solids treatment. Combining the composition data from Chapter 2 for a sensitivity analysis, process conditions from Chapter 3 for an updated process model, and LCA approach from Chapter 4, this chapter compares economic and environmental impacts of biofuel production from wastewater greases.

Because wastewater grease disposal methods vary greatly based on location and municipal regulations (Long et al., 2012; Wiltsee, 1998), several disposal scenarios were analyzed in the analysis presented in this chapter. Common practices are disposal at a landfill, incinerator, or anaerobic digester (Long et al., 2012). The degradation of organic material in a landfill emits biogas which is primarily composed of methane (CH_4) (Jungbluth et al., 2007; Kabouris et al., 2009; Long et al., 2012; USEPA, 2015b), which accounts toward GHG emissions (IPCC, 2013).

Landfill gas collection and anaerobic digestion offer ways to reduce the GHG emissions from the CH_4 by flaring or cogenerating heat and electricity; these processes convert the CH_4 to biogenic CO_2, thus reducing GHG emissions. Recent laboratory and LCA research has focused on anaerobic co-digestion of GTW with residual biosolids such as sewage sludge (Gough et al., 2013; Long et al., 2012; Razaviarani et al., 2013; Silvestre et al., 2011); however, extracting the brown grease lipids for biodiesel

production and anaerobic digestion of the wastewater has been reported to produce more usable energy than anaerobic digestion alone (Lopez et al., 2014; Tu & McDonnell, 2015). Also, the variability of the feedstock could affect the microbiological activity in the anaerobic digester, which is sensitive to changes in feedstock composition, particularly long-chain fatty acids (Lopez et al., 2014). Separating brown grease lipids from GTW for biodiesel production has several potential benefits for waste management facilities, including reducing the volume of GTW that is processed for disposal and replacing petroleum diesel combustion by a renewable fuel while potentially reducing their carbon footprint.

This chapter investigated the potential economic and environmental benefits of producing biodiesel from wastewater greases. A techno-economic analysis and life cycle impact assessment were performed on a theoretical small-scale biofuel production facility located at a Pennsylvania regional wastewater grease collection facility. This study assumed the biofuel facility produced two fuels: the main product biodiesel and a co-product biobunker (a biogenic heavy fuel oil). The wastewater grease composition results from the longitudinal study presented in Chapter 2 were incorporated into a sensitivity analysis to determine the effect of brown grease production on GHG emissions and potential for economic profits. Because there are multiple solid waste disposal treatment options, GHG emissions were determined for solid waste disposal at an anaerobic digester, incinerator, or landfill. This research also included a comparison between the GHG emissions of current wastewater grease disposal and biofuel production.

5.2. Techno-Economic Analysis of Biofuel Production from Wastewater Greases

A techno-economic model of biofuel production from wastewater greases was developed by Environmental Fuel Research, LLC during Phase I of an EPA SBIR project that was used to estimate the economic feasibility of the GTW biodiesel process and to produce a process inventory (quantities of all input and output material and energy flows) that was necessary for the LCA in the following section. In this project, we modified this model to incorporate data from the longitudinal study to predict process performance for converting both GTW and SSG to biodiesel. The process was divided into five sections depicted in the block flow diagram in Figure 5.1. Process flow diagrams, equipment lists, raw material requirements, utility usage, and waste generation were calculated for each of these sections.

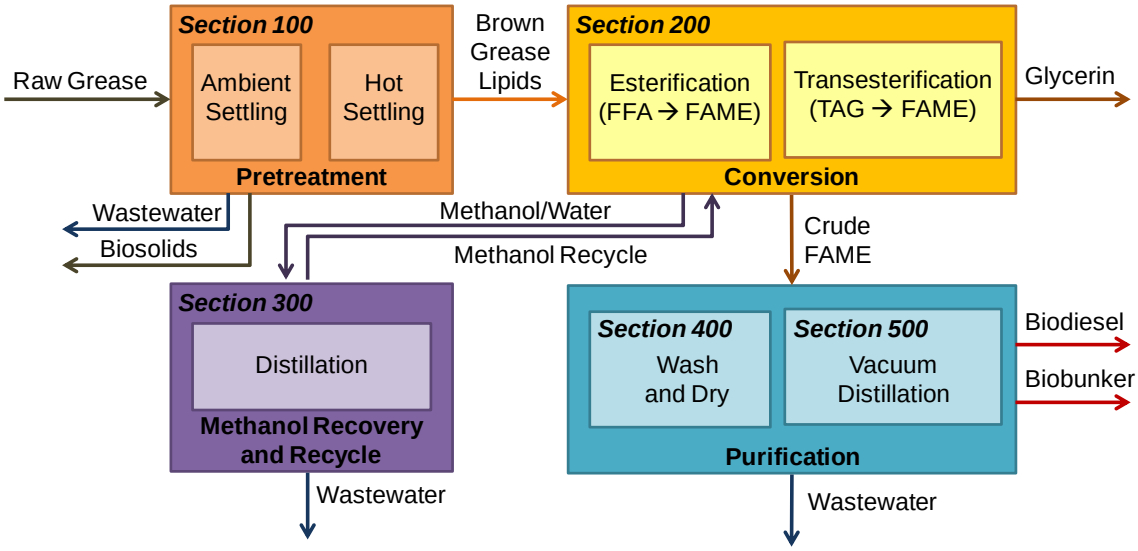


Figure 5.1: Block flow diagram for biofuel process from wastewater greases indicating major processing steps and flow of intermediates from wastewater grease to biodiesel. Each block contains a block number that is used to organize stream and equipment information for operations within that section of the process.

The biofuel production process five sections included: (100) pretreatment – dewatering and separating brown grease from raw grease, (200) conversion – esterification and transesterification of brown grease lipids with methanol to form fatty acid methyl esters (FAME), (300) methanol recovery – distillation of vapor exhaust from reactor to recycle methanol, (400) water washing crude FAME, (500) vacuum distillation of FAME to biodiesel using a wiped film evaporator. Process flow diagrams, equipment lists, raw material requirements, utility usage, and waste generation were predicted for each of these sections. .

5.2.1. Pretreatment

In the pretreatment section 100, the raw grease first underwent ambient temperature dewatering that allowed the raw grease to settle for separation of the float layer from the secondary wastewater layer and sediment layer. SSG collected at wastewater resource recovery facilities (WRRFs) is similar to the top floating layer of raw GTW; therefore, initial filtering and dewatering steps were not needed for SSG. Acid was added to lower the pH of the float layer and SSG and transferred to a hot settling tank for brown grease lipid extraction. After another settling step, the brown grease lipids were decanted, filtered and ready for conversion. The fraction of wastewater that was acidified during lipid extraction was neutralized with a base and transported with the rest of the settled wastewater to wastewater treatment. The waste solids were collected and disposed at a solid waste treatment facility. Various disposal options were analyzed and will be discussed in the LCA Section 5.3. The amount of brown grease lipids, floating solids, sediments, and wastewater were all variable for GTW and seasonally dependent for SSG; the longitudinal study data was used to

determine the sensitivity of the biofuel production, economics, and environmental impacts using a Monte Carlo simulation.

5.2.2. Conversion

In the conversion section 200, the brown grease lipids were assumed to compose a mixture of free fatty acids (FFA), triglycerides (TAG), and un-saponifiable materials. The percent mass of the FFA was determined using the data found in the longitudinal study. The un-saponifiable material content was set to a constant 5% mass of the brown grease and the TAG was determined as the remaining percent mass. FFA was first converted (esterified) into FAME before the TAG conversion (transesterification) to avoid converting the FFA into soaps. The brown grease was pumped and heated to 120 °C where it was combined with fresh methanol and 0.2% by mass sulfuric acid as catalyst. The FFA was esterified in a bubble column reactor which assumed 90% conversion of FFA into FAME at 120 °C and ambient pressure. Throughout the reaction methanol vapor was fed into the reactor. Because the reactor operated above the boiling point of water, the water produced with the reaction was vaporized and exited the reactor as a vapor with un-reacted methanol. The water and methanol were condensed for methanol recovery discussed in section 300. The crude FAME product from the esterification and the un-reacted FFA and TAG continued to a second reactor for the transesterification of TAG into FAME. The feed was cooled to 85 °C, and a 30% by mass solution of sodium hydroxide in methanol was used as a catalyst. The transesterified reaction assumed 90% conversion of TAG into FAME. There was a small amount of impure glycerin produced from the transesterification reaction; the glycerin by-product was composed of about equal mass percentages of glycerin, methanol, and

sodium hydroxide and about 10% by mass salt. Instead of purifying the small amount, the material was considered as waste and transported for wastewater treatment.

5.2.3. Methanol Recovery

In the methanol recovery section 300, the methanol and water vapor exiting the esterification and transesterification reactors were condensed and distilled. The distillation operated with a reflux ratio of 1.5, at ambient pressure, with reboiler temperature of approximately 100 °C and condenser temperature of approximately 60 °C. The distillate was 99% mass methanol with 1% mass water which was recycled for re-use in the conversion. The bottoms consisted of 94% by mass water and 6% by mass methanol which was transported for wastewater treatment.

5.2.4. Purification

In the purification sections 400 and 500, three steps were performed: (1) washing of crude biodiesel, (2) drying/heating of the crude, and (3) vacuum distillation. The crude FAME after transesterification was neutralized with a sulfuric acid water wash of 99% by mass water and 1% by mass sulfuric acid. After the wash, the water was transported for wastewater treatment and the crude FAME was heated to 190 °C to remove any remaining water or methanol prior to the vacuum distillation. Vacuum distillation was used to purify the crude, high-sulfur FAME into ASTM-quality biodiesel. The distillation operated at 0.001 atm and 190°C. The distillate yield was 90% by mass which was the product biodiesel; the residue (un-distilled) was a high-sulfur, viscous material that was considered as a bio-based bunker fuel (biobunker). The process analysis here assumed that this process was sufficient to produce biodiesel that meets ASTM specifications.

5.2.5. Economics

The cost of raw materials and utilities were determined using market prices for each material (Table 5.1).

Table 5.1: Expenditures and revenues for biofuel production from wastewater greases.

Cost of Utilities (CUT)	GTW (MJ/kgRawGrease)	SSG Cool (MJ/kgRawGrease)	SSG Temperate (MJ/kgRawGrease)	SSG Warm (MJ/kgRawGrease)	$/GJ	Source
Cooling Water	0.058	0.714	0.394	0.128	$0.354	TBWS (2009)[1]
Hot water	0.001	0.016	0.013	0.011	$6.670	TBWS (2009)[1]
Low pressure steam	0.069	0.808	0.523	0.283	$7.780	TBWS (2009)[1]
Hot oil	0.011	0.137	0.074	0.024	$7.500	TBWS (2009)[1]
Electricity	0.011	0.128	0.069	0.023	$16.800	TBWS (2009)[1]

Cost Raw Materials (CRM)	GTW (kg/kgRawGrease)	SSG Cool (kg/kgRawGrease)	SSG Temperate (kg/kgRawGrease)	SSG Warm (kg/kgRawGrease)	$/kg	Source
Raw grease	1.000	1.000	1.000	1.000	-$0.016	DELCORA VI[2]
Polymer for grease separation	6.09E-05	0.000E+00	0.00E+00	0.00E+00	$3.850	alibaba.com[3]
Methanol	0.002	0.028	0.015	0.005	$0.666	ICIS[4]
Acid catalyst (H_2SO_4)	0.002	0.024	0.022	0.020	$0.207	ICIS[4]
Base catalyst (NaOH)	0.002	0.023	0.020	0.017	$0.564	ICIS[4]
Wash water	0.067	0.826	0.446	0.147	$0.000	TBWS (2009)[1]
Process water for steam and cooling	0.107	1.302	0.758	0.307	$0.000	TBWS (2009)[1]
Acid neutrlization of wastewater (H_2SO_4)	0.000	0.004	0.002	0.001	$0.207	ICIS[4]
Oxidation stabilizer	6.16E-06	7.602E-05	4.10E-05	1.35E-05	$9.259	Springboard biodiesel[5]

Sale of Products/By-products (Revenue) & Cost of Wastes (CWT)	GTW (kg/kgRawGrease)	SSG Cool (kg/kgRawGrease)	SSG Temperate (kg/kgRawGrease)	SSG Warm (kg/kgRawGrease)	$/kg	Source
Biodiesel	0.026	0.327	0.176	0.058	-$0.955	Alternative fuels data center[6]
Renewable fuel incentive					-$0.295	EPA[7]
Biobunker	0.004	0.047	0.025	0.008	-$0.468	Bunkerindex.com[8]
Wastewater from grease	0.609	0.000	0.000	0.000	$0.004	DELCORA X[2]
Sediments from ambient separator	0.281	0.000	0.000	0.000	$0.016	DELCORA VI[2]
Wastewater from hot separator	0.032	0.340	0.327	0.359	$0.004	DELCORA X[2]
Wet solids from hot separator	0.080	0.673	0.872	0.985	$0.016	DELCORA VI[2]
Wastewater with methanol	0.001	0.018	0.010	0.003	$0.008	DELCORA IV[2]
Crude glycerin	0.001	0.011	0.006	0.002	$0.009	TBWS (2009)[1]
Waste washwater	0.070	0.859	0.464	0.153	$0.008	DELCORA IV[2]

1. (Turton et al., 2009); 2.(DELCORA, 2013); 3. (Alibaba Group, 2014); 4.(ICIS, 2014);
5. (Springboard Biodiesel, 2014); 6.(USDOE, 2014); 7. (USEPA, 2015a); 8. (Bunker Index, 2014)

Table 5.1 shows costs of the raw materials, utilities, and waste disposal and selling prices for raw materials, waste removal, biodiesel, and biobunker. The heat needed for the separation, conversion, and methanol recovery was provided by steam production from natural gas, while the vacuum distillation used heating oil for energy. The negative values represent the revenue from biofuel production while the black positive values represent expenditures. The sum of the red values was the selling price per kg of material. The cost of the waste solids disposal was kept the same regardless of disposal option; realistically, the cost of disposal at a landfill or anaerobic digester may be different than at the wastewater treatment plant for incineration (DELCORA is a WRRF that incinerates waste greases and the roman numerals represent different wastewater types).

The cost of operating labor (COL) was determined using the assumption that four operators were on duty per shift with 4.5 shifts needed to account for continuous operation including weekends, holidays, and vacation. The annual operator salary was assumed to be $50,000 per year and the total annual cost for operators was $900,000. Operating labor was a fixed cost that did not vary with the size of the process. Because operating labor costs were fixed at nearly one million dollars per year, designing a process to receive larger amounts of wastewater grease and produce larger amounts of biodiesel will lead to larger revenues and better profitability (i.e. there is an economy of scale). For most chemical manufacturing processes, raw material costs are the largest contributor to the cost of manufacturing.

The fixed capital investment of the equipment (FCI) was dependent on the plant capacity. Therefore, multiple scenarios were studied for the sensitivity analysis to

analyze the effects that plant capacity and feed rate have on the quantity of biodiesel produced and the economics of the process. The equipment was sized and priced according to the material balances and used a program developed for Drexel University senior design projects.

The cost of manufacturing (COM) and annualized capital (AC) were calculated in order to determine the annual cash flow (CF). The COM was determined using the Equation 5.1.

$$COM = 0.18 * FCI + 2.76 * COL + 1.23 * (CUT + CWT + CRM) \qquad (Eq\ 5.1)$$

The annualized capital that was used for calculating depreciation was approximated using Equation 5.2.

$$AC = \frac{FCI}{7} \qquad (Eq\ 5.2)$$

The annual after tax cash flow, *CF*, was determined using a taxation rate of 42% and Equation 5.3.

$$CF = (RFS - COM) * (1 - 0.42) - AC * 0.42 \qquad (Eq\ 5.3)$$

If the annual after tax cash flow was positive, then the simple payback period was calculated using Equation 5.4.

$$Payback = \frac{FCI}{CF} \qquad (Eq\ 5.4)$$

If the annual cash flow was negative, then the payback period was undefined and the process was considered economically unfeasible.

Table 5.2 presents a base case scenario for GTW and each season of SSG that assumed an average composition of GTW and seasonal average composition of SSG found in data from the longitudinal study (Chapter 2).

Table 5.2: Economic base case for GTW composition average and SSG composition averages by season.

Variable	Abbreviation	Unit	GTW	SSG Cool	SSG Temperate	SSG Warm
Revenue from sales	RFS	$	$ 7,257,959	$ 6,098,918	$ 3,452,511	$ 1,305,001
Cost raw materials	CRM	$	$ 516,987	$ 520,615	$ 369,248	$ 247,408
Cost of utilities	CUT	$	$ 119,536	$ 134,091	$ 84,384	$ 42,110
Cost of waste treatment	CWT	$	$ 1,236,912	$ 255,012	$ 259,490	$ 255,697
Cost of operating labor	COL	$	$ 900,000	$ 900,000	$ 900,000	$ 900,000
Cost of manufacturing	COM	$	$ 5,399,816	$ 4,147,916	$ 3,906,104	$ 3,699,578
Annualized capital	AC	$/y	$ 485,311	$ 432,511	$ 432,511	$ 432,511
Fixed capital investment	FCI	$	$ 3,397,175	$ 3,027,578	$ 3,027,578	$ 3,027,578
Cash flow	CF	$/y	$ 1,281,554	$ 1,313,235	$ (81,429)	$ (1,207,200)
Payback period	PB	y	2.65	2.31	N/A	N/A

Variable	Abbreviation	Unit	GTW	SSG Cool	SSG Temperate	SSG Warm
Biodiesel produced	BD	gal/y	745,776	874,910	481,345	160,906
Revenue from sales	RFS	$/galBD	$ 9.73	$ 6.97	$ 7.17	$ 8.11
Cost raw materials	CRM	$/galBD	$ 0.69	$ 0.60	$ 0.77	$ 1.54
Cost of utilities	CUT	$/galBD	$ 0.16	$ 0.15	$ 0.18	$ 0.26
Cost of waste treatment	CWT	$/galBD	$ 1.66	$ 0.29	$ 0.54	$ 1.59
Cost of operating labor	COL	$/galBD	$ 1.21	$ 1.03	$ 1.87	$ 5.59
Cost of manufacturing	COM	$/galBD	$ 7.24	$ 4.74	$ 8.11	$ 22.99
Annualized capital	AC	$/galBD	$ 0.65	$ 0.49	$ 0.90	$ 2.69
Fixed capital investment	FCI	$/galBD	$ 4.56	$ 3.46	$ 6.29	$ 18.82
Cash flow	CF	$/galBD	$ 1.72	$ 1.50	$ (0.17)	$ (7.50)
Payback period	PB	y	2.65	2.31	N/A	N/A

For GTW, a flow rate of 5,000 gal/h raw GTW was used and for SSG a flow rate of 500 gal/h raw SSG from SCB was used. The GTW base case scenario and the SSG cool season showed similar economic factors with payback periods of about 2.5-3 y. The SSG seasonal data per year represents having a cool climate all year long; however in climates with seasonal transitions, the cool months may only occur approximately one third of the

year. The SSG temperate and warm season data both have negative cash flows because the cost of manufacturing was larger than the revenue from sales.

5.3. Life Cycle Assessment of Biofuel Production from Wastewater Greases

5.3.1. Goal and Scope

Life cycle assessment (LCA) was initially performed on the biodiesel production from GTW to analyze the sensitivity of brown grease lipid content on the environmental impacts as discussed in Chapter 4 (Dufour & Iribarren, 2012; Hums, Cairncross, et al., 2016; Tu & McDonnell, 2015). The key finding was that the waste disposal of the residual wastes (primarily wet biosolids) after the brown grease lipid extraction had the highest GHG emissions and was sensitive to the brown grease lipid content (Hums, Cairncross, et al., 2016; Tu & McDonnell, 2015). However, the disposal of the residual wastes was an already occurring process regardless of biodiesel production. Therefore, the goal of this life cycle analysis was to compare "business as usual" to the production of biofuels. "Business as usual" referred to the disposal of raw GTW and SSG wastewater to WRRF and biosolids, including brown grease, to solid waste treatment. This scenario was then compared to biofuel production; the brown grease was extracted from the biosolids and converted into biodiesel and biobunker while the biosolids were sent to solid waste treatment and wastewater sent to wastewater treatment.

The disposal of the biosolids varies depending on the region with common disposal at landfills, anaerobic digesters, or incinerators (Long et al., 2012). These disposal options have waste treatment options as well. In this study, the biosolids waste disposal scenarios analyzed were:

- Anaerobic digestion
    - Biogas upgrading to a biogenic compressed natural gas (CNG)
    - Biogas cogeneration of electricity and heat
- Incineration
    - Not including heat recovery
    - Including heat recovery
- Landfilling
    - No methane gas collection
    - Landfill gas collection with cogeneration of electricity and heat
    - Landfill gas flaring

The raw grease disposal options for business as usual and biofuel production are shown in Figure 5.2. The global warming potential (GWP_{100}) was determined using IPCC 2013 data (IPCC, 2013). The GWP_{100} values and sources used in the LCA are shown in Table 5.3.

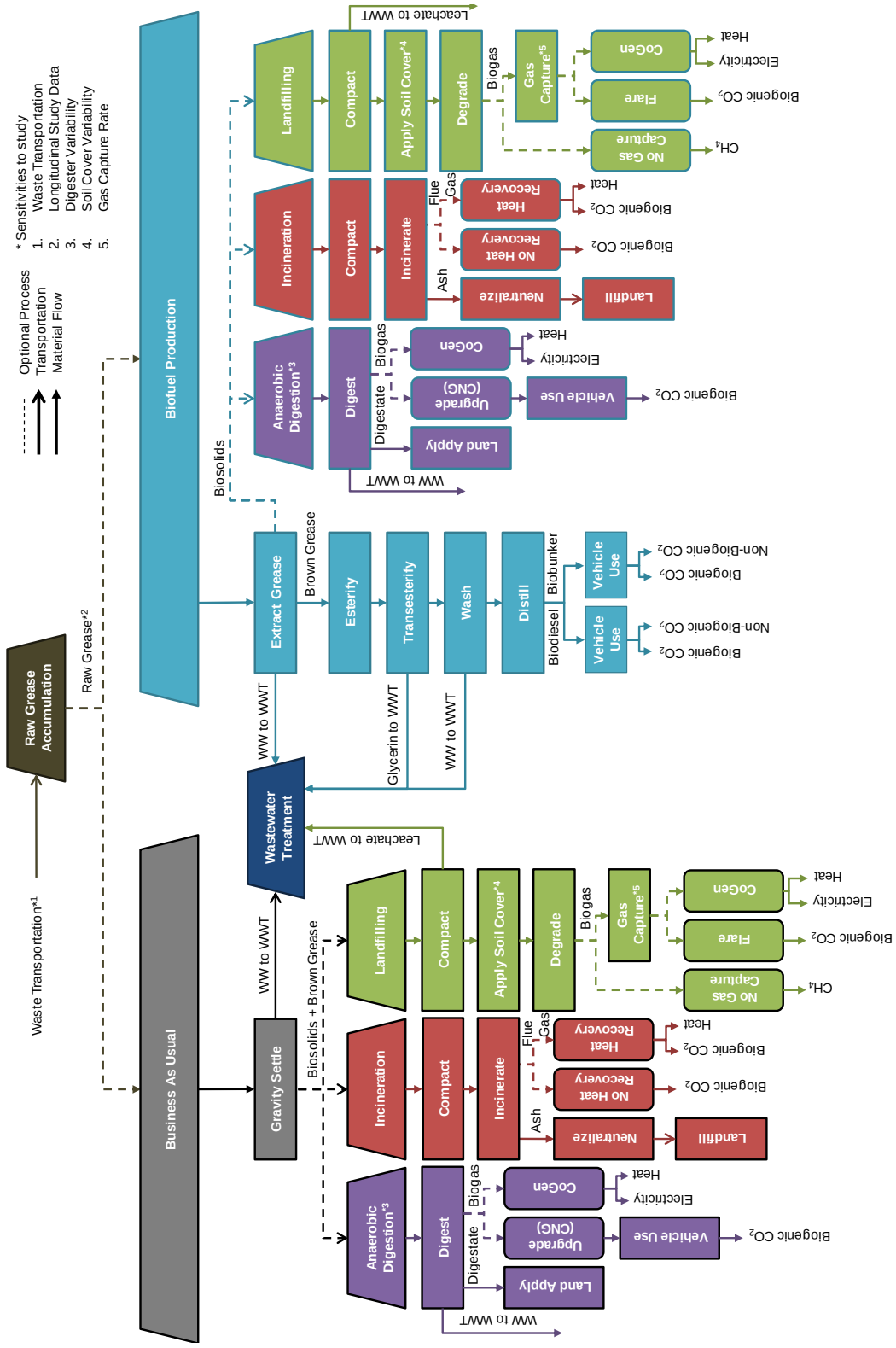


Figure 5.2: Disposal options for raw grease including business as usual and biofuel production.

Table 5.3: Global warming potentials for materials used in LCA disposal analysis.

	Amount	Unit	GWP_{100} (gCO_2eq/Unit)	Process	Source, Database	Source Name
GREENHOUSE GASES						
Non-biogenic carbon dioxide	1	g	1		IPCC 2013[1]	
Methane	1	g	30		IPCC 2013[1]	
Nitrous oxide	1	g	298		IPCC 2013[1]	
INPUTS						
Utilities						
Process water	1	kg	0.00139	Cooling water in biofuel production	SimaPro[2], Ecoinvent[3]	Water, decarbonised, at plant/RER U
Electricity	1	MJ	195	All scenarios	GREET2014[4]	Electricity RFC mix
Steam production from natural gas	1	MJ	86.6	Biofuel production	GREET2014[4]	Steam production from north american natural gas
Natural gas	1	MJ	69.3	Anaerobic digestion	GREET2014[4]	North American natrural gas
Low-sulfur diesel (LSD)	1	MJ	92.9	For equipment in incineration, anaerobic digestion, and landfill	GREET2014[4]	Low-sulfur diesel
Transportation						
Combination truck	1	tkm	93.0	All scenarios	SimaPro[2], USLCI[5]	Transport, combination truck, diesel powered/US
Materials						
Methanol	1	kg	782	Reactant in biodiesel production	SimaPro[2], Ecoinvent[3]	Methanol, at regional storage/CH U
Sodium hydroxide	1	kg	1017	Catalyst in biodiesel production	SimaPro[2], Ecoinvent[3]	Sodium hydroxide, 50% in H2O, production mix, at plant/RER U
Sulfuric acid	1	kg	1769	Catalyst in biodiesel production	SimaPro[2], Ecoinvent[3]	Sulphuric acid, liquid, at plant/RER U
Wash water	1	kg	0.651	Biodiesel production	SimaPro[2], Ecoinvent[3]	Deionised, at plant/CH U
Ammonia for neutralization	1	kg	2.01	Ash neutralization in incineration	SimaPro[2], Ecoinvent[3]	Ammonia, liquid, at regional storehouse/CH U
Lime for biosolids neutralization	1	kg	476	Biofuel production, incineration	GREET2014[4]	Lime production from limestone
Lubricating oil for cogeneration equipment	1	kg	894	Anaerobic digestion, landfill	SimaPro[2], Ecoinvent[3]	Lubricating oil, at plant/RER U
OUTPUTS						
Materials						
Wastewater treatment	1	kg	0.124	All scenarios	SimaPro[2], Ecoinvent[3]	Treatment, sewage, to wastewater treatment, class 3/CH U
Lubricating oil disposal from cogeneration equipment	1	kg	2845	Anaerobic digestion, landfill	SimaPro[2], Ecoinvent[3]	Disposal, used mineral oil, 10% water, to hazardous waste incineration/CH U
Emissions						
Biodiesel combustion	1	MJ	3.75	Combustion in biofuel production	Hums (current study)	
Biobunker combustion	1	MJ	4.00	Combustion in biofuel production	Hums (current study)	
Credits						
Low-sulfur diesel (LSD)	1	MJ	-92.9	Displaced in biofuel production	GREET2014[4]	Low-sulfur diesel
Bunker fuel	1	MJ	-92.1	Displaced in biofuel production	GREET2014[4]	Residual oil (petroleum) from crude oil for use as a marine fuel
Electricity	1	MJ	-195	Displaced in cogeneration	GREET2014[4]	Electricity RFC mix
Natural gas	1	MJ	-69.3	Displaced in incineration and cogeneration	GREET2014[4]	North American natrual gas
Petroleum CNG	1	MJ	-76.4	Displaced in anaerobic digestion gas upgrade	GREET2014[4]	CNG from North American natural gas
Phosphorus in fertilizer	1	kgP	-1800	Displaced in anaerobic digestion digestate disposal	Møller et al.[6]	Phosphorus for fertilizer
Nitrogen in fertilizer	1	kgN	-8900	Displaced in anaerobic digestion digestate disposal	Møller et al.[6]	Nitrogen for fertilizer
Potassium in fertilizer	1	kgK	-960	Displaced in anaerobic digestion digestate disposal	Møller et al.[6]	Potassium for fertilizer

1. (IPCC, 2013); 2. (PRéConsultants, 2014); 3. (Jungbluth et al., 2007); 4. (Argonne National Laboratory, 2014); 5. (USNREL, 2012); 6. (Møller et al., 2009)

In this analysis, system expansion was used for the treatment of co-products shown as "Credits" in Table 5.3. When electricity and heat were co-produced in the anaerobic digestion and landfilling cogeneration scenarios, we assumed the same displacement of grid electricity and natural gas. In anaerobic digestion, the upgrading of

biogas to CNG displaced the petroleum CNG and the digestate produced displaced the need for phosphorus, nitrogen, and potassium in conventional fertilizers. Natural gas was displaced in the incineration with heat recovery scenario. With the production of biofuels, the biodiesel displaced low-sulfur diesel (LSD) and its co-product biobunker displaced petroleum bunker fuel.

5.3.2. System Boundaries

There are two main system boundaries for this life cycle impact assessment (LCIA): (1) business as usual where brown grease was disposed of with the biosolids and (2) biofuel production with extraction of brown grease from biosolids and conversion into biodiesel and biobunker. GTW and SSG had slightly different collection and separation processes as described in Figure 5.3 for (A) GTW and (B) SSG.

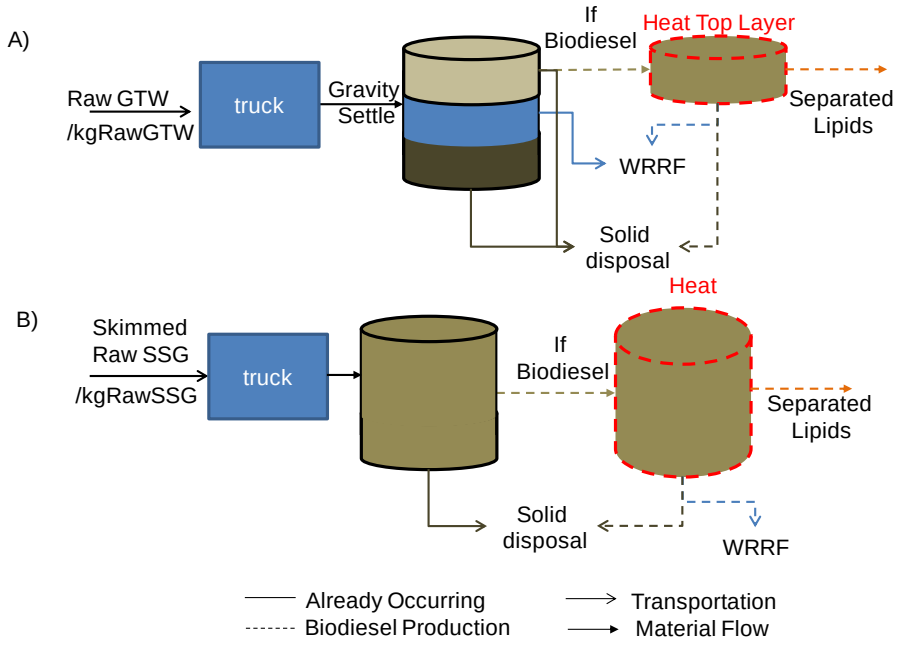


Figure 5.3: Raw grease disposal for (A) GTW and (B) SSG. Business as usual (solid lines) is compared to biofuel production which includes brown grease lipid extraction for biodiesel and biobunker (indicated by dotted lines).

For GTW, the secondary wastewater was transported to a WRRF and the sediments and floating solids were transported to solid waste disposal facilities. For SSG, the raw grease was already skimmed at the primary settling tanks so the amount of water and sediments was not included in this analysis; therefore, there was no ambient settling required as compared to GTW. The key difference between business as usual and biofuel production was that the brown grease lipids were sent with the biosolids to the treatment facilities.

5.3.2.1. Raw Grease Accumulation/Settling Facility

For the LCA, it was assumed that the raw grease was transported an average of 286 km by combination truck to the accumulation/separation facilities. For GTW, the raw float grease separated and sediments were separated from the wastewater. The waste solids (both scenarios) and brown grease lipids (business as usual) were transported 50 km by combination truck to one of the solid waste disposal options. The wastewater was transported 50 km by combination truck to a WRRF. For SSG, all of the waste solids (both scenarios) and brown grease lipids (business as usual) were transported from the accumulation facility to one of the solid waste disposal options.

The combination truck had a GWP_{100} emission of 93 gCO_2eq/tkm. The tkm represents a metric ton-km traveled; therefore, the weight of the transported material (in metric tons) was multiplied by the transportation distance.

5.3.2.2. Anaerobic Digestion (AD)

Anaerobic digestion is a disposal method that offers products and co-products such as biogenic source for compressed natural gas (CNG), cogeneration of heat and

electricity, and using the digested matter as fertilizer. Figure 5.4 and Table 5.4 display the system boundary and the inventory for the disposal process, respectively.

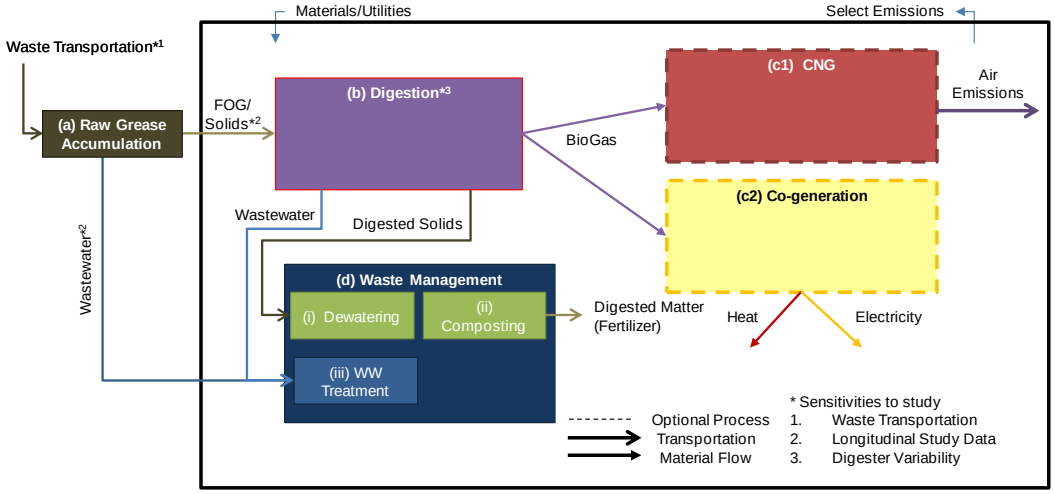


Figure 5.4: Anaerobic digestion system boundary.

Table 5.4: Anaerobic digestion inventory for base cases of GTW and SSG with business as usual and biofuel production options.

Anaerobic Digestion	Unit	Business as Usual				Biofuel Production			
		GTW	SSG Cool	SSG Temperate	SSG Warm	GTW	SSG Cool	SSG Temperate	SSG Warm
INPUTS									
Raw Grease									
Biosolids	kg/kgRawGrease	0.39	0.59	0.78	0.92	0.36	0.26	0.46	0.57
Brown grease lipids	kg/kgRawGrease	0.03	0.40	0.21	0.07	0.00	0.00	0.00	0.00
Total Solids	kg/kgRawGrease	0.42	0.99	0.99	0.99	0.36	0.26	0.46	0.57
Utilities									
Electricity - anaerobic digester	MJ/kgRawGrease	0.005	0.01	0.01	0.01	0.004	0.00	0.01	0.01
Electricity - gas upgrade	MJ/kgRawGrease	0.068	0.10	0.14	0.16	0.063	0.05	0.08	0.10
Natural gas	MJ/kgRawGrease	0.249	0.59	0.59	0.59	0.214	0.16	0.27	0.34
LSD for digestate application	MJ/kgRawGrease	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01
Transportation									
Combination truck for digestate	tkm/kgRawGrease	0.02	0.04	0.04	0.04	0.01	0.01	0.02	0.02
Materials									
Lubricating oil for cogeneration equipment	kg/kgRawGrease	0.000	6.04E-05	7.91E-05	9.36E-05	0.000	2.68E-05	4.66E-05	5.79E-05
OUTPUTS									
Materials									
Digestate	kg/kgRawGrease	0.35	0.89	0.86	0.84	0.30	0.22	0.38	0.47
Lubricating oil disposal from cogeneration equipment	kg/kgRawGrease	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Emissions									
Methane - gas upgrade	kg/kgRawGrease	8.09E-04	1.23E-03	1.61E-03	1.91E-03	7.48E-04	5.47E-04	9.51E-04	1.18E-03
Credits									
Electricity - cogeneration	MJ/kgRawGrease	0.42	0.64	0.84	1.00	0.39	0.29	0.50	0.62
Natural Gas - cogeneration	MJ/kgRawGrease	0.73	1.11	1.45	1.72	0.67	0.49	0.85	1.06
Petroleum CNG - upgrade	MJ/kgRawGrease	1.30	1.98	2.59	3.07	1.20	0.88	1.53	1.90
Phosphorus in fertilizer	kg/kgRawGrease	0.94	2.36	2.28	2.22	0.79	0.58	1.01	1.25
Nitrogen in fertilizer	kg/kgRawGrease	0.04	0.10	0.10	0.09	0.03	0.02	0.04	0.05
Potassium in fertilizer	kg/kgRawGrease	0.09	0.23	0.23	0.22	0.08	0.06	0.10	0.12

The wet biosolids portion of the raw waste greases was transported to an anaerobic digester. The operation of the digester was assumed using the EcoInvent database (Jungbluth et al., 2007). The electricity consumption was 0.011 MJ/kg Biosolids and the natural gas heat input was 0.59 MJ/kg Biosolids. Literature data were used to characterize the anaerobic digestion of GTW and brown grease fats, oils, and greases to analyze the variability of the total solids (TS), volatile solids (VS), and CH_4 generation rate (Table 5.5).

Table 5.5: Biosolids and brown grease properties used in anaerobic digestion.

Materials	Unit	Base Case	Low	High	References
TS ratio wet solids	gTS/kgWetSolids	97	70	124	(Wang et al., 2013) (Li et al., 2011)
TS ratio brown grease	gTS/kgBrownGrease	968	951	985	
VS ratio wet solids	gVS/kgWetSolids	92	70	114	
VS ratio brown grease	gVS/kgBrownGrease	955	938	972	
CH_4 generation rate wet solids	m^3/kgVSWetSolids	0.454	0.155	0.752	(Wang et al., 2013) (Li et al., 2011) (Kabouris et al., 2009)
CH_4 generation rate brown grease	m^3/kgVSBrown Grease	0.574	0.155	0.993	

After digestion the residual biosolids (digestate) and water was used as fertilizer; it was assumed the digestate and water was transported 50 km to a field. The application of digestate to the field by a vehicle required 0.71 L diesel/metric ton of digestate (Berglund & Börjesson, 2006). The fertilizer nutrients (nitrogen, phosphorus, and potassium) in the digestate were 2.65 g N/kg digestate, 0.11 gP/kg digestate, and 0.26 gK/kg digestate (Møller et al., 2009). These amounts of nutrients were then used to offset the production of other fertilizers shown in Table 5.3.

The biogas, a mixture of primarily CH_4 (65% vol) and CO_2 was collected (Jungbluth et al., 2007). The biogas could be upgraded to product gas which was composed of 96% vol CH_4 (CNG) or cogenerated to produce heat and electricity. In the CNG scenario, there was an electricity consumption of 1.8 MJ/m^3 Product gas (Jungbluth et al., 2007). The product gas had a collection efficiency of 67% and the remaining 33% volume of biogas (65% vol CH_4 and remaining CO_2) was treated as a waste emission to the atmosphere (Jungbluth et al., 2007). Product substitution was used for the displacement of nonrenewable CNG by product biogas.

In the cogeneration scenario, there was lubricant consumption and disposal with a consumption rate of 0.03 g lubricant/ MJ Biogas in (MJin) (Jungbluth et al., 2007). The heat generation was considered to be 0.55 MJ/MJin and electricity generation was considered to be 0.32 MJ/MJin (Jungbluth et al., 2007). The product substitution for the generated heat was natural gas and the electricity substitution was Reliability First Corporation (RFC) region grid electricity (USEIA, 2015a).

5.3.2.3. Incineration

Incineration is potentially beneficial because instead of allowing the raw grease to degrade to produce and emit CH_4, the waste is burned and converted to biological CO_2. Incineration of waste solids occurs at DELCORA which is a WRRF in Chester, PA where RRWM disposes of GTW. This facility does not recovery energy; however, heat recovery is an option presented in this study. Figure 5.5 and Table 5.6 display the system boundary and the inventory for the disposal process, respectively.

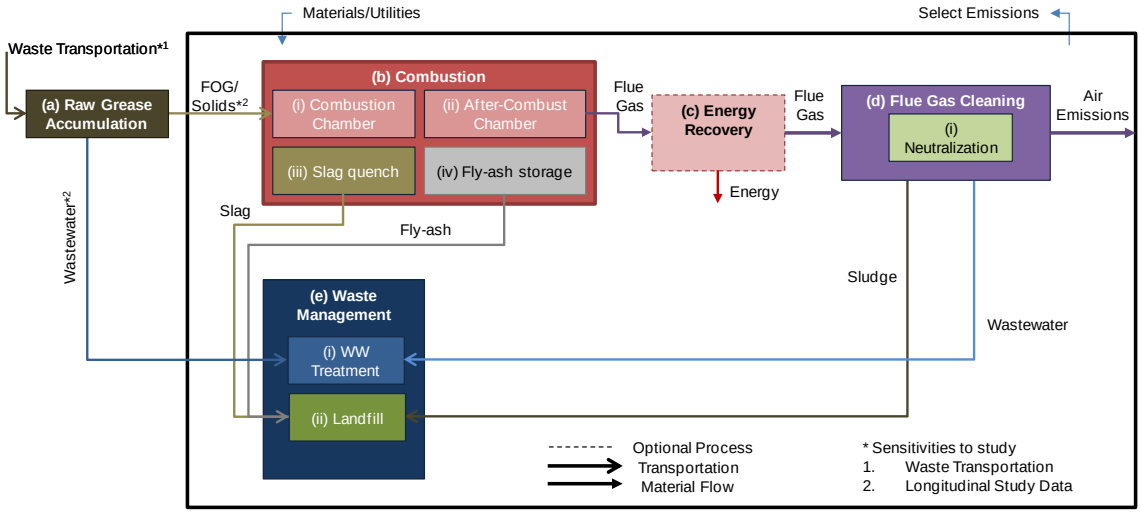


Figure 5.5: Incineration system boundary.

Table 5.6: Incineration inventory for base cases of GTW and SSG with business as usual and biofuel production options.

Incineration	Unit	Business as Usual				Biofuel Production			
		GTW	SSG Cool	SSG Temperate	SSG Warm	GTW	SSG Cool	SSG Temperate	SSG Warm
INPUTS									
Raw Grease									
Biosolids	kg/kgRawGrease	0.39	0.59	0.78	0.92	0.36	0.26	0.46	0.57
Brown grease lipids	kg/kgRawGrease	0.03	0.40	0.21	0.07	0.00	0.00	0.00	0.00
Total solids	kg/kgRawGrease	0.42	0.99	0.99	0.99	0.36	0.26	0.46	0.57
Utilities									
Electricity	MJ/kgRawGrease	0.10	0.25	0.25	0.25	0.09	0.07	0.11	0.14
LSD for compacting	MJ/kgRawGrease	5.70E-04	7.58E-04	1.32E-03	1.64E-03	5.70E-04	7.58E-04	1.32E-03	1.64E-03
Transportation									
Combination truck for incineration waste disposal	tkm/kgRawGrease	7.12E-04	9.48E-04	1.65E-03	2.05E-03	7.12E-04	9.48E-04	1.65E-03	2.05E-03
Materials									
Ammonia for incineration waste neutralization	kg/kgRawGrease	9.49E-04	2.24E-03	2.24E-03	2.24E-03	8.14E-04	5.96E-04	1.04E-03	1.29E-03
Lime for incineration waste neutralization	kg/kgRawGrease	2.02E-04	2.69E-04	4.67E-04	5.80E-04	2.02E-04	2.69E-04	4.67E-04	5.80E-04
OUTPUTS									
Materials									
Incineration waste	kg/kgRawGrease	0.01	0.02	0.03	0.04	0.01	0.02	0.03	0.04
Credits									
Natural gas - w/ heat recovery	MJ/kgRawGrease	1.01	11.818	6.56	2.42	0.12	0.164	0.29	0.355

The LCA of the incineration process utilized a report by the Swedish Environmental Research Institute on incineration of solid waste materials (Sundqvist, 1999). The overall incineration process included the consumption of: diesel for

compacting, ammonia and lime for neutralization of waste solids, and electricity for powering fans. These consumption rates are shown in Table 5.7; the corresponding GWP_{100} value are shown in Table 5.3.

Table 5.7: Materials consumed in incineration process.

Incineration Emissions	Quantity	
Electricity	0.25	MJ electricity/kg biosolids
Diesel for compacting	0.04	MJ diesel/kg biosolids
Ammonia	0.0011	kg Ammonia/kg biosolids
Lime	0.014	kg Lime/kg biosolids

After incineration, there was approximately 0.18 kg ash/kg biosolids that were transported 50 km by combination truck to a landfill.

In the incineration with heat recovery option, there was an assumed 85% heat recovery efficiency. The biosolids are assumed to have a lower heating value (LHV) of 2 MJ/kg Biosolids and 37.71 MJ/kg Brown Grease (considered for business as usual scenario). The energy produced in this option displaced natural gas.

5.3.2.4. Landfilling

Three options were considered for the landfilling of the biosolids: (1) no gas collection, (2) flaring of landfill gas, and (3) cogeneration of heat and electricity from landfill gas. Figure 5.6 and Table 5.8 display the system boundary and the inventory for the disposal process, respectively.

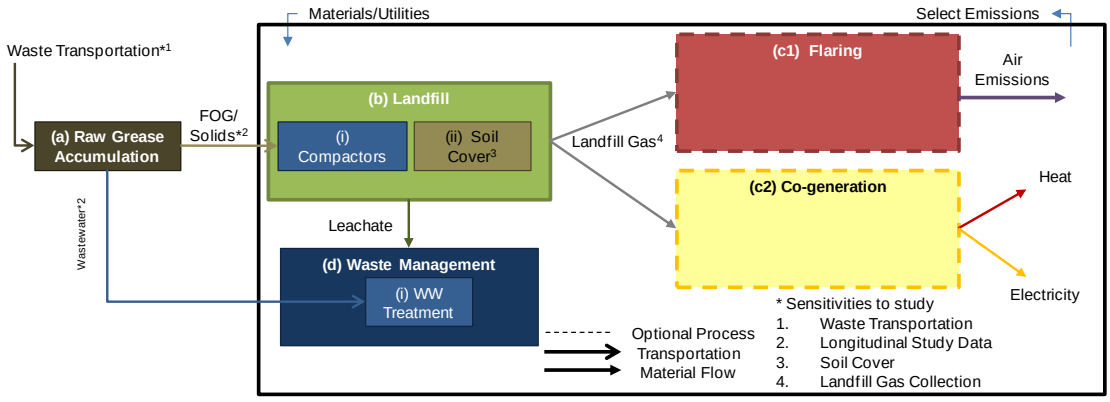


Figure 5.6: Landfill system boundary.

Table 5.8: Landfill inventory for base cases of GTW and SSG with business as usual and biofuel production options.

Incineration	Unit	Business as Usual				Biofuel Production			
		GTW	SSG Cool	SSG Temperate	SSG Warm	GTW	SSG Cool	SSG Temperate	SSG Warm
INPUTS									
Raw Grease									
Biosolids	kg/kgRawGrease	0.39	0.59	0.78	0.92	0.36	0.26	0.46	0.57
Brown grease lipids	kg/kgRawGrease	0.03	0.40	0.21	0.07	0.00	0.00	0.00	0.00
Total solids	kg/kgRawGrease	0.42	0.99	0.99	0.99	0.36	0.26	0.46	0.57
Utilities									
Electricity	MJ/kgRawGrease	0.10	0.25	0.25	0.25	0.09	0.07	0.11	0.14
LSD for compacting	MJ/kgRawGrease	5.70E-04	7.58E-04	1.32E-03	1.64E-03	5.70E-04	7.58E-04	1.32E-03	1.64E-03
Transportation									
Combination truck for incineration waste disposal	tkm/kgRawGrease	7.12E-04	9.48E-04	1.65E-03	2.05E-03	7.12E-04	9.48E-04	1.65E-03	2.05E-03
Materials									
Ammonia for incineration waste neutralization	kg/kgRawGrease	9.49E-04	2.24E-03	2.24E-03	2.24E-03	8.14E-04	5.96E-04	1.04E-03	1.29E-03
Lime for incineration waste neutralization	kg/kgRawGrease	2.02E-04	2.69E-04	4.67E-04	5.80E-04	2.02E-04	2.69E-04	4.67E-04	5.80E-04
OUTPUTS									
Materials									
Incineration waste	kg/kgRawGrease	0.01	0.02	0.03	0.04	0.01	0.02	0.03	0.04
Credits									
Natural gas - w/ heat recovery	MJ/kgRawGrease	1.01	11.818	6.56	2.42	0.12	0.164	0.29	0.355

The report from the Swedish Environmental Protection Agency was also used for the landfill gas emissions (Sundqvist, 1999). This source was useful because it had detailed equations on calculating the land emissions specifically for food waste and fats to determine the CH_4 emissions generated from the degrading material.

The biosolids were treated as food waste with the same composition as described in the report; in the report food waste had 24% fat, 13% protein, 18% degradable carbohydrates, 21% cellulose, 6% nondegradable organic material, and a chlorine content of 0.4% all as a portion of dry waste. For this study, the biodiesel scenario removed the fats (brown grease) from the rest of the material. The percentage of fat for the business as usual scenario was determined using the brown grease lipid content in the floating solids layer. Table 5.9 depicts the chosen proteins, degradable carbohydrates, cellulose, and nondegradable organic material on a % dry material basis for the average composition of GTW.

Table 5.9: Biosolids composition assumptions for GTW base case.

	Dry Basis			Wet Basis		
Landfill Assumptions	**Unit**	**Biofuel Waste Scenario**	**Business As Usual Waste Scenario**	**Unit**	**Biofuel Waste Scenario**	**Business As Usual Waste Scenario**
Moisture	% moisture	78%	73%	% moisture	78%	73%
Dry material	% dry material	22%	27%	% dry material	22%	27%
Fat	% of dry material	0%	31%	% of total material	0.00%	8.31%
Protein	% of dry material	19%	11%	% of total material	4.25%	3.05%
Degradable carbs	% of dry material	24%	16%	% of total material	5.36%	4.40%
Cellulose	% of dry material	27%	19%	% of total material	6.03%	5.21%
Nondegradable organic material	% of dry material	12%	4%	% of total material	2.68%	1.16%
Chlorine	% of dry material	0.40%	0.40%	% of total material	0.09%	0.11%

Each of the components in Table 5.9 have a certain amount of degradation (alpha) and methane ratio (beta) as defined by Sundqvist (Sundqvist, 1999) in Table 5.10. The

biosolids composition data in Table 5.9 was multiplied by the amount of dry biosolids to determine the percent composition on a total wet solids basis. The alpha and beta values and carbon contents were determined using the weighted average.

Table 5.10: Compound properties for landfill degradation.

Compound	Degredation yield (alpha) kg degraded C/ kg C	Methane ratio in gas (beta), $CH_4/(CH_4+CO_2)$ kmol/kmol	Carbon content
Fat*	100%	0.82	4.0%
Protein*	100%	0.52	4.9%
Degradable carbs, starch, sugar*	100%	0.50	40.0%
Cellulose*	70%	0.50	7.0%
Humus, lignin*	0%	0.49	8.0%
Chlorine*	0%	0.00	0.0%
Weighted average for biofuel scenario	75%	0.50	16.0%
Weighted average for business as usual	86%	0.61	13.0%

*(Sundqvist, 1999)

The amount of CH_4 emitted from the landfill was approximated using gamma, the oxidation yield of CH_4 in the soil cover and eta, the amount of recovered CH_4. The oxidation of the CH_4 varies greatly so a base case of 15% CH_4 oxidized/CH_4 transported through the soil was chosen (Spokas et al., 2011). The thickness of the soil layer, soil type, and climate all contribute to the soil oxidation; therefore, a uniform distribution of 4%-60% oxidation was analyzed based from a study for a landfill gas emissions model (Spokas et al., 2011). The collection of the landfill gas changes depending on location. The U.S. EPA model uses an average rate of collection is 75% with a range between 50-95% collection (USEPA, 2015b). For the sensitivity analysis discussed in the next

section, a triangular distribution was used with this range and the likeliest value was 75% for the gas collection rate. The amount of landfill gas was calculated according to the Swedish landfill report (Sundqvist, 1999) in Figure D.1 of Appendix D.1. The flaring and no gas capture scenarios are depicted in the appendix figure. The cogeneration of heat and electricity was determined using the same process described in the anaerobic digestion section which utilized the EcoInvent database procedure. The leachate had potential to be used as a fertilizer or algae substrate, but in this scenario, the leachate was transported 50 km for disposal at a WRRF.

5.3.2.5. Biofuel Production

The biofuel process model described in Section 5.2 was used to determine the materials and energy required for the production of biodiesel. Figure 5.7 and display the system boundary and the inventory for the disposal process, respectively.

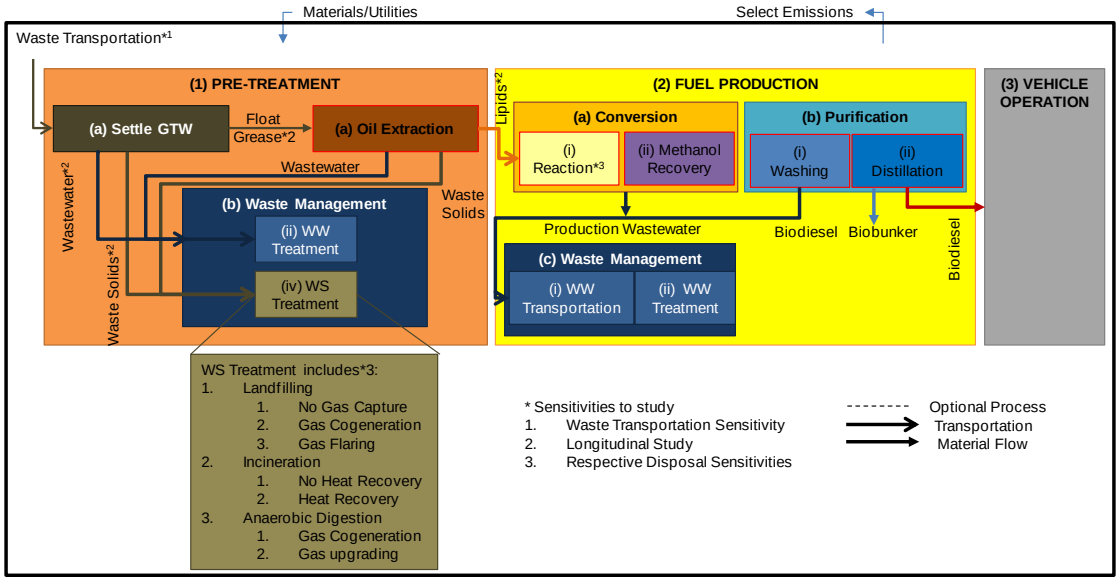


Figure 5.7: Biofuel production system boundary.

Table 5.11: Biofuel production inventory for base cases of GTW and SSG.

Biodiesel Process	Unit	Biofuel Production			
		GTW	SSG Cool	SSG Temperate	SSG Warm
INPUTS					
Raw Grease					
Brown grease lipids	kg/kgRawGrease	0.030	0.396	0.213	0.070
Utilities					
Process water	MJ/kgRawGrease	0.059	0.730	0.407	0.139
Electricity	MJ/kgRawGrease	0.011	0.128	0.069	0.023
Steam production from natural gas	MJ/kgRawGrease	0.102	1.202	0.763	0.397
Materials					
Methanol	kg/kgRawGrease	0.002	0.028	0.015	0.005
Sodium hydroxide	kg/kgRawGrease	0.002	0.023	0.020	0.017
Sulfuric acid	kg/kgRawGrease	0.002	0.024	0.022	0.020
Wash water	kg/kgRawGrease	0.067	0.826	0.446	0.147
Process water	kg/kgRawGrease	0.107	1.302	0.758	0.307
Lime for neutralization	kg/kgRawGrease	0.000	4.05E-03	0.002	7.30E-04
OUTPUTS					
Materials					
Wastewater from conversion	kg/kgRawGrease	0.001	0.018	0.010	0.003
Wash water	kg/kgRawGrease	0.070	0.859	0.464	0.153
Glycerin	kg/kgRawGrease	0.001	0.011	0.006	0.002
Emissions					
Biodiesel combustion	MJ/kgRawGrease	0.026	0.327	0.176	0.058
Biobunker combustion	MJ/kgRawGrease	0.004	0.047	0.025	0.008
Credits					
Low-sulfur diesel (LSD)	MJ/kgRawGrease	0.026	0.327	0.176	0.058
Bunker fuel	MJ/kgRawGrease	0.004	0.047	0.025	0.008

The final stage of the biodiesel life cycle was the combustion of the fuel. The biodiesel lower heating value (LHV) was 37.8 MJ/kg. Assuming the biodiesel was methyl oleate, the biodiesel has a total carbon content of 77%. However, the biodiesel is composed of 19 carbon molecules; 18 of the carbons are attributed to the bio-based brown grease lipids which are renewable and when combusted considered zero emission. The other carbon is from the methanol which is derived from fossil sources. Therefore, the GWP_{100} of the combustion of biodiesel was considered $1/19^{th}$ of the total CO_2

emissions or 4% non-biogenic carbon content. The CO_2 emissions were then be calculated using Equation 5.5.

$$\frac{gCO_2}{MJ\ Fuel} = \frac{44\ gCO_2}{12\ gC} \times \frac{1}{LHV\left(\frac{MJ}{kg}\right)} \times \%C_{Non-bio} \times \frac{1000g}{kg} \qquad (Eq\ 5.5)$$

The biodiesel combustion was 3.75 g CO_2eq/MJ Fuel. The biobunker was composed primarily of un-distilled biodiesel and un-saponifiable fatty acids. Assuming a LHV of 33 MJ/kg, non-biogenic carbon content of 5%, Equation 5.5 was used to calculate the combustion emissions; the combustion emissions for biobunker was approximately 4 g CO_2eq/MJ Fuel.

It was assumed that for every MJ of biodiesel and biobunker produced, one MJ of LSD and heavy bunker fuel was displace; these fuels have a GWP_{100} of 93 and 92 g CO_2eq/MJ Fuel, respectively.

5.3.3. Global Warming Potential Base Case

For the GTW and each SSG season, base cases for GTW and SSG were analyzed prior to running Monte Carlo. The composition was determined as the average value of GTW and each season of SSG determined through the longitudinal study. Table 5.12 describes the composition parameters and process size used for the base cases. Since raw GTW is composed of the floating solids and grease layer, the wastewater layer, and the sediments layer, there is a larger volume compared to the SSG. SSG collected at scum concentration building is already partially dewatered and separated from the rest of the wastewater and sediments; therefore, the SSG floating layer volume was assumed as 99%.

Table 5.12: Average raw grease composition data from longitudinal study.

Variable	Unit	GTW	SSG Warm	SSG Temp	SSG Cool
Raw grease feed rate	gal/h	5,000	500	500	500
Floating layer volume	%vol	11%	99%	99%	99%
Wet sediments volume	%vol	31%	1%	1%	1%
Moisture content of wet sediments	kg/kg	80%	80%	80%	80%
Lipid content in float layer	%mass	32%	7%	22%	40%
Wet solids content of float layer	%mass	55%	62%	59%	44%
Moisture content of wet solids	%mass	60%	60%	60%	60%
FFA content of lipids	%mass	75%	77%	78%	75%

The floating layer and sediment volumes for GTW were the average results from measuring the layers of GTW in the special tank. For SSG and GTW, the lipid content in the float layer and wet solids content of float layer were the average masses determined from the grease lipid extraction mentioned in Chapter 2. The FFA content of the brown grease lipids was the average values determined from titration of the extracted lipids.

5.3.3.1. 100-Year Global Warming Potential Base Case of GTW

The base case for GTW used the average values from the longitudinal study of the 500 gal tank. Two processes were studied (1) biofuel production and (2) business as usual, and seven options for disposal of waste solids were considered. The GWP_{100} of the waste solids disposal options and biofuel production are shown in Table 5.13.

Table 5.13: Global warming potential base case results for GTW disposal scenarios.

A) Biofuel Production	Unit	Landfill Gas Flare	Landfill Gas Cogen	Landfill Gas Uncollected	Incineration w/ HR	Incineration w/o HR	Anaerobic Digestion CNG	Anaerobic Digestion Cogen
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	2.91	2.91	2.91	2.91	2.91	2.91	2.91
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	529.25	522.64	2077.34	19.67	19.67	53.79	19.22
Waste Solids Credit	gCO_2eq/ kgRawGrease	0.00	-34.60	0.00	-8.56	0.00	-99.09	-130.06
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	529.25	488.04	2077.34	10.90	19.67	-45.30	-110.84
Biofuel Production w/o Credits	gCO_2eq/ kgRawGrease	17.71	17.71	17.71	17.71	17.71	17.71	17.71
Biofuel Production Credit	gCO_2eq/ kgRawGrease	-104.68	-104.68	-104.68	-104.68	-104.68	-104.68	-104.68
Biofuel Production w/ Credit	gCO_2eq/ kgRawGrease	-86.97	-86.97	-86.97	-86.97	-86.97	-86.97	-86.97
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***576.47***	***569.85***	***2124.55***	***66.88***	***66.88***	***101.00***	***66.43***
Total Credits	***gCO_2eq/ kgRawGrease***	***-104.68***	***-139.28***	***-104.68***	***-113.24***	***-104.68***	***-203.77***	***-234.74***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***471.79***	***430.57***	***2019.87***	***-46.36***	***-37.80***	***-102.77***	***-168.31***
B) Business As Usual								
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	2.77	2.77	2.77	2.77	2.77	2.77	2.77
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	530.99	523.28	2245.52	22.63	22.63	59.79	22.41
Waste Solids Disposal Credit	gCO_2eq/ kgRawGrease	0.00	-34.86	0.00	-70.29	0.00	-107.86	-141.34
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	530.99	488.41	2245.52	-47.66	22.63	-48.07	-118.93
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***560.36***	***552.64***	***2274.89***	***52.00***	***52.00***	***89.16***	***51.78***
Total Credits	***gCO_2eq/ kgRawGrease***	***0.00***	***-34.86***	***0.00***	***-70.29***	***0.00***	***-107.86***	***-141.34***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***560.36***	***517.78***	***2274.89***	***-18.29***	***52.00***	***-18.71***	***-89.57***

Table 5.13 is divided between (A) Biofuel production and (B) Business as usual. Under the biofuel production, the first row shows the GWP_{100} of the waste collection and the second row represents the secondary wastewater disposal. For each disposal option regardless of biofuel production or business as usual, the waste collection was the same value because the amount of material transported was the same. The wastewater treatment was different between biofuels production and business as usual because in the biofuel production pretreatment stage, more water was extracted in the pretreatment than

was able to be collected from gravity settling alone. The remaining contributors to GWP_{100} were waste solids, biofuel production, and total, which are split into three rows each: (1) w/o Credit, (2) Credit, and (3) w/ Credit. The waste solids disposal and biodiesel production stages both produced products or by-products that may displace fossil-derived process; such as when biodiesel is produced, the credit is an avoided amount of LSD. The "w/o Credit" row is the sub-process GWP_{100} without including a credit of an avoided process, the "Credit" row is the credit, and the "w/ Credits" row is the sum of the first and second row.

In all but one of the disposals studied for GTW, the biofuel production total GWP_{100} including credit had a lower value than business as usual because of the credits from biodiesel substituting for petroleum diesel and biobunker substituting for heavy fuel oil. By far, the lowest (most negative) GWP_{100} corresponded to the waste disposal by anaerobic digestion at -90 g CO_2eq/kg Raw Grease for business as usual and -168 g CO_2eq/kg Raw Grease for biofuel production. The highest GWP_{100} corresponded to landfilling without gas collection with greater than 2,000 g CO_2eq/kg Raw Grease for both business as usual and biofuel production; this high GWP_{100} was due to the landfill emitting a significant amount of CH_4, which is a potent GHG. These base case values will change depending on the composition of the raw GTW as discussed in the sensitivity analysis explored in Chapter 5.4.

The only case in which business as usual had a low GWP_{100} was incineration with heat recovery, in which case the GWP_{100} for business as usual and biofuel production are nearly the same; this similarity was because the brown grease lipids in GTW have a

similar lower heating value to biodiesel. The brown grease lipids contributed to heat generation in incineration that was then recovered and displaced natural gas.

Anaerobic digestion with cogeneration of heat and electricity offered the lowest GWP_{100} for both biofuel production and business as usual. Cogeneration was also effective at lowering the GWP_{100} because of the credit from avoided grid electricity. The GWP_{100} for electricity production was 195 g CO_2eq/MJ Electricity; this impact could be a lower value as electricity production shifts from coal and other non-renewable sources toward bio-based, renewable sources. The electricity GWP_{100} credit in the future may not be as significant depending upon local electricity production.

5.3.3.2. 100-Year Global Warming Potential Base Case of SSG

There was seasonal variability to the brown grease lipid content of the SSG which could affect the biofuel production process. Three base case scenarios were studied for SSG to analyze the GWP_{100} of biofuel production during the cool season with high brown grease lipid content (Table 5.14), temperate season with moderate brown grease lipid content (Table 5.15), and warm season with low brown grease lipid content (Table 5.16).

Table 5.14: Global warming potential base case results for SSG cool season disposal scenarios.

A) Biofuel Production	Unit	Landfill Gas Flare	Landfill Gas Cogen	Landfill Gas Uncollected	Incineration w/ HR	Incineration w/o HR	Anaerobic Digestion CNG	Anaerobic Digestion Cogen
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/kgRawGr	1.62	1.62	1.62	1.62	1.62	1.62	1.62
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	526.07	521.24	2075.94	14.65	14.65	39.35	14.06
Waste Solids Credit	gCO_2eq/ kgRawGrease	0.00	-34.17	0.00	-11.38	0.00	-72.49	-95.15
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	526.07	487.07	2075.94	2.97	14.65	-33.14	-81.09
Biofuel Production w/o Credits	gCO_2eq/ kgRawGrease	208.94	208.94	208.94	208.94	208.94	208.94	208.94
Biofuel Production Credit	gCO_2eq/ kgRawGrease	-1292.19	-1292.19	-1292.19	-1292.19	-1292.19	-1292.19	-1292.19
Biofuel Production w/ Credit	gCO_2eq/ kgRawGrease	-1083.25	-1083.25	-1083.25	-1083.25	-1083.25	-1083.25	-1083.25
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***763.23***	***758.40***	***2313.10***	***251.80***	***251.80***	***276.50***	***251.21***
Total Credits	***gCO_2eq/ kgRawGrease***	***-1292.19***	***-1326.37***	***-1292.19***	***-1303.58***	***-1292.19***	***-1364.68***	***-1387.34***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***-528.96***	***-567.97***	***1020.91***	***-1051.77***	***-1040.39***	***-1088.18***	***-1136.12***
B) Business As Usual								
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	547.14	528.90	1738.11	53.16	53.16	110.05	53.07
Waste Solids Disposal Credit	gCO_2eq/ kgRawGrease	0.00	-37.38	0.00	-818.81	0.00	-172.84	-223.89
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	547.14	491.51	1738.11	-765.65	53.16	-62.80	-170.82
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***573.79***	***555.54***	***1764.76***	***79.80***	***79.80***	***136.69***	***79.71***
Total Credits	***gCO_2eq/ kgRawGrease***	***0.00***	***-37.38***	***0.00***	***-818.81***	***0.00***	***-172.84***	***-223.89***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***573.79***	***518.16***	***1764.76***	***-739.01***	***79.80***	***-36.15***	***-144.18***

Table 5.15: Global warming potential base case results for SSG temperate season disposal scenarios.

A) Biofuel Production	Unit	Landfill Gas Flare	Landfill Gas Cogen	Landfill Gas Uncollected	Incineration w/ HR	Incineration w/o HR	Anaerobic Digestion CNG	Anaerobic Digestion Cogen
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	1.57	1.57	1.57	1.57	1.57	1.57	1.57
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	531.85	523.43	2078.13	25.45	25.45	68.39	24.43
Waste Solids Credit	gCO_2eq/ kgRawGrease	0.00	-35.03	0.00	-19.79	0.00	-125.98	-165.36
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	531.85	488.39	2078.13	5.17	25.45	-57.60	-140.93
Biofuel Production w/o Credits	gCO_2eq/ kgRawGrease	128.75	128.75	128.75	128.75	128.75	128.75	128.75
Biofuel Production Credit	gCO_2eq/ kgRawGrease	-695.08	-695.08	-695.08	-695.08	-695.08	-695.08	-695.08
Biofuel Production w/ Credit	gCO_2eq/ kgRawGrease	-566.33	-566.33	-566.33	-566.33	-566.33	-566.33	-566.33
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***688.76***	***680.34***	***2235.04***	***182.36***	***182.36***	***225.30***	***181.34***
Total Credits	***gCO_2eq/ kgRawGrease***	***-695.08***	***-730.11***	***-695.08***	***-714.87***	***-695.08***	***-821.07***	***-860.44***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***-6.32***	***-49.78***	***1539.96***	***-532.50***	***-512.72***	***-595.77***	***-679.10***

B) Business As Usual								
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	547.65	529.40	2147.76	53.38	53.38	127.51	52.96
Waste Solids Disposal Credit	gCO_2eq/ kgRawGrease	0.00	-37.39	0.00	-454.77	0.00	-218.80	-285.58
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	547.65	492.02	2147.76	-401.39	53.38	-91.29	-232.62
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***574.29***	***556.05***	***2174.40***	***80.02***	***80.02***	***154.15***	***79.60***
Total Credits	***gCO_2eq/ kgRawGrease***	***0.00***	***-37.39***	***0.00***	***-454.77***	***0.00***	***-218.80***	***-285.58***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***574.29***	***518.66***	***2174.40***	***-374.75***	***80.02***	***-64.65***	***-205.98***

Table 5.16: Global warming potential base case results for SSG warm season disposal scenarios.

A) Biofuel Production	Unit	Landfill Gas Flare	Landfill Gas Cogen	Landfill Gas Uncollected	Incineration w/ HR	Incineration w/o HR	Anaerobic Digestion CNG	Anaerobic Digestion Cogen
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	1.72	1.72	1.72	1.72	1.72	1.72	1.72
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	535.14	524.67	2079.37	31.61	31.61	84.94	30.34
Waste Solids Credit	gCO_2eq/ kgRawGrease	0.00	-35.52	0.00	-24.58	0.00	-156.48	-205.38
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	535.14	489.15	2079.37	6.42	31.61	-71.54	-175.03
Biofuel Production w/o Credits	gCO_2eq/ kgRawGrease	64.48	64.48	64.48	64.48	64.48	64.48	64.48
Biofuel Production Credit	gCO_2eq/ kgRawGrease	-229.07	-229.07	-229.07	-229.07	-229.07	-229.07	-229.07
Biofuel Production w/ Credit	gCO_2eq/ kgRawGrease	-164.60	-164.60	-164.60	-164.60	-164.60	-164.60	-164.60
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***627.93***	***617.47***	***2172.17***	***124.41***	***124.41***	***177.73***	***123.14***
Total Credits	***gCO_2eq/ kgRawGrease***	***-229.07***	***-264.59***	***-229.07***	***-253.65***	***-229.07***	***-385.55***	***-434.45***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***398.86***	***352.87***	***1943.10***	***-129.24***	***-104.66***	***-207.82***	***-311.31***
B) Business As Usual								
Waste Collection	gCO_2eq/ kgRawGrease	26.60	26.60	26.60	26.60	26.60	26.60	26.60
Wastewater Disposal	gCO_2eq/ kgRawGrease	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Waste Solids Disposal w/o Credit	gCO_2eq/ kgRawGrease	548.13	529.88	2243.44	53.51	53.51	141.19	52.88
Waste Solids Disposal Credit	gCO_2eq/ kgRawGrease	0.00	-37.39	0.00	-167.82	0.00	-254.80	-333.91
Waste Solids Disposal w/ Credit	gCO_2eq/ kgRawGrease	548.13	492.49	2243.44	-114.31	53.51	-113.62	-281.03
Total w/o Credits	***gCO_2eq/ kgRawGrease***	***574.77***	***556.52***	***2270.08***	***80.15***	***80.15***	***167.83***	***79.52***
Total Credits	***gCO_2eq/ kgRawGrease***	***0.00***	***-37.39***	***0.00***	***-167.82***	***0.00***	***-254.80***	***-333.91***
Total w/ Credits	***gCO_2eq/ kgRawGrease***	***574.77***	***519.13***	***2270.08***	***-87.67***	***80.15***	***-86.97***	***-254.38***

The overall trends in the results for GWP_{100} of SSG processing are similar to those for GTW processing. For the business as usual processing, the GWP_{100} for each waste disposal option was nearly independent of the season; however season had a large effect on the GWP_{100} for the biofuel production process. For any of the seasons, the total GWP_{100} of biofuel production with any of the disposal scenarios (except for incineration

with heat recovery) was lower than that of the business as usual. Generally, the landfill scenario had the highest GWP_{100}. For the cold season biofuel production, the landfill gas flaring and cogeneration scenarios had a negative GWP_{100} because the amount of LSD avoided was higher than the amount of CH_4 emitted to the atmosphere. Anaerobic digestion with cogeneration of heat and electricity in all seasons had the lowest GPW_{100}. It appears that if biodiesel were not produced, the best alternative would be to incinerate the waste and recover the heat that was generated during the incineration. However, if biofuel was produced, anaerobic digestion of the wet solids with cogeneration would be the best disposal option because the combination has the lowest GWP_{100}.

5.4. Sensitivity and Variability

Oracle Crystal Ball (Oracle, 2014) was used to run a Monte Carlo analysis to identify the effects primarily of raw grease composition on the biodiesel production process, economics of the process, and the global warming potential of business as usual and biofuel production. The simulation was run for 10,000 trials changing different parameters that were distributions fitted to the longitudinal study data.

Table 5.17: Scenarios for Monte Carlo simulation.

Study #	Label	Distribution Data	Code	Dewatering Equipment	Plant Capacity		Feed Rate		%vol Float Grease	%vol Sediments	%mass Lipids	%mass Wet Solids	%mass FFA
					Un-fixed/Fixed	gal/h	Shape	gal/h	Shape	Shape	Shape	Shape	Shape
1	GTW	A1	A1-UV	Yes	Un-fixed	250-10,000	Uniform	250-10,000	Normal	Lognormal	Lognormal	Fixed	MinEx
2	GTW	A1	A1-FV	Yes	Fixed	5,000	Uniform	250-10,000	Normal	Lognormal	Lognormal	Fixed	MinEx
3	GTW	A1	A1-F5	Yes	Fixed	5,000	Fixed	5,000	Normal	Lognormal	Lognormal	Fixed	MinEx
4	GTW	A10	A10-UV	Yes	Un-fixed	250-10,000	Uniform	250-10,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
5	GTW	A10	A10-FV	Yes	Fixed	5,000	Uniform	250-10,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
6	GTW	A10	A10-F5	Yes	Fixed	5000	Fixed	5,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
7	GTW	A100	A100-UV	Yes	Un-fixed	250-10,000	Uniform	250-10,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
8	GTW	A100	A100-FV	Yes	Fixed	5,000	Uniform	250-10,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
9	GTW	A100	A100-F5	Yes	Fixed	5,000	Fixed	5,000	Lognormal	Lognormal	Lognormal	Fixed	Normal
10	SSG	Warm	W-UV	No	Un-fixed	25-1,000	Uniform	25-1,000	Fixed	Fixed	Lognormal	Lognormal	Normal
11	SSG	Warm	W-FV	No	Fixed	500	Uniform	250-10,000	Fixed	Fixed	Lognormal	Lognormal	Normal
12	SSG	Warm	W-F5	No	Fixed	500	Fixed	500	Fixed	Fixed	Lognormal	Lognormal	Normal
13	SSG	Temperate	T-UV	No	Un-fixed	25-1,000	Uniform	25-1,000	Fixed	Fixed	Triangular	Normal	Normal
14	SSG	Temperate	T-FV	No	Fixed	500	Uniform	250-10,000	Fixed	Fixed	Triangular	Normal	Normal
15	SSG	Temperate	T-F5	No	Fixed	500	Fixed	500	Fixed	Fixed	Triangular	Normal	Normal
16	SSG	Cool	C-UV	No	Un-fixed	25-1,000	Uniform	25-1,000	Fixed	Fixed	Lognormal	Normal	MinEx
17	SSG	Cool	C-FV	No	Fixed	500	Uniform	250-10,000	Fixed	Fixed	Lognormal	Normal	MinEx
18	SSG	Cool	C-F5	No	Fixed	500	Fixed	500	Fixed	Fixed	Lognormal	Normal	MinEx

Table 5.17 displays the scenarios that were analyzed. For GTW, three different distributions of the raw grease composition were studied. The reason for the three distribution sets was to analyze the effect of aggregation of GTW. The longitudinal study data (A1) was approximately one truckload of GTW and this data was used to estimate aggregating ten truckloads (A10) and aggregating 100 truckloads (A100); these truckloads are discussed in the data fitting section 5.4.1. Also, in the longitudinal study, SSG lipid content had a correlation to the temperature; therefore three distributions of data were studied for warm, temperate, and cool season SSG compositions. The distribution shapes chosen for the composition variables will be discussed for GTW and SSG in the following sections.

The plant capacity of the biofuel production facility was also analyzed. The economic feasibility of biofuel production depends on the scale of the plant and the feed rate of the incoming raw grease. Therefore, three plant capacity and feed rate scenarios were studied. The first was a variable (unfixed) plant capacity with variable feed rate entering the plant; in this scenario, the equipment size and utility costs vary depending on the amount of raw grease entering the biofuel plant. Second, a fixed plant capacity was designed while the operating capacity varied based on feed rate. This scenario best represents the operation of real-world plant. For GTW, a plant capacity for raw grease feed rate of 5,000 gal/h was chosen. This plant capacity corresponds to raw grease processing of 37 MMgalGTW/y and biodiesel production of 0.75 MMgalGTWBiodiesel/y. For SSG, the brown grease lipids and solids were more concentrated; so a smaller feed rate of raw SSG would produce about the same amount of

biofuels. A fixed rate of 500 gal/h was chosen for SSG. This plant capacity corresponds to raw grease processing of 3.7 MMgalSSG/y and biodiesel production of 0.87 MMgalSSGBiodiesel/y. The third scenario represented a fixed plant capacity and a fixed feed rate of 5,000 gal/h and 500 gal for GTW and SSG, respectively. This scenario was used to analyze the impacts associated with the grease composition and disposal assumptions without the variability of plant capacity and feed rate. In general, the term "assumptions" refer to the fitted distribution variables studied in the sensitivity analysis; the list of assumptions is shown in Table 5.18.

Table 5.18: Assumptions for Monte Carlo simulation.

	Variables	Description	GTW/SSG	Waste Option	Distribution	Range
Solid Waste Disposal	CH_4 Gen BG	Methane generation in brown grease	GTW/SSG	Anaerobic Digestion	Uniform	0.155-0.752 m3/kg VS brown grease
	CH_4 Gen WS	Methane generation in wet solids	GTW/SSG	Anaerobic Digestion	Uniform	0.155-0.752 m3/kg VS wet solids
	TS BG	Total solids in brown grease	GTW/SSG	Anaerobic Digestion	Uniform	70-295 gTS/kg brown grease
	TS WS	Total solids in wet solids	GTW/SSG	Anaerobic Digestion	Uniform	70-205 gTS/kg wet solids
	VS BG	Volatile solids in brown grease	GTW/SSG	Anaerobic Digestion	Uniform	938-972 gVS/kg brown grease
	VS WS	Volatile solids in wet solids	GTW/SSG	Anaerobic Digestion	Uniform	951-985 gVS/kg wet solids
	Oxidized CH4 in soil	Methane oxidation in soil	GTW/SSG	Landfill	Uniform	4%-60%
	Recovered methane	Methane captured at landfill	GTW/SSG	Landfill	Triangular	50-95%; Likliest: 75%
Raw Grease Properties	%m FFA	Mass percent of free fatty acids	GTW/SSG	ALL	Dependent on scenario.	
	%m lipids	Mass percent of lipids	GTW/SSG	ALL		
	%m wet solids	Mass percent of wet solids in top layer	SSG	ALL		
	%v sediments	Volume percent of sediments	GTW	ALL		
	%Vol float layer	Volume percent of float layer	GTW	ALL		
	Raw grease transport	Distance traveled to waste-to-biodiesel	GTW/SSG	ALL	Normal	Mean: 286 km; SD: 117 km
Plant Size	Feed rate	Rate of waste grease entering system	GTW	ALL	Uniform	250-10,000 gal/h depending on scenario
	Feed rate	Rate of waste grease entering system	SSG	ALL	Uniform	25-1,000 gal/h depending on scenario

Uniform distributions were chosen for the anaerobic digestion variables and CH_4 oxidation in soil at a landfill due to the small, diverse range of data given in literature; therefore it was best to give each value in the range the same probability. The recovered CH_4 captured at a landfill used a triangular distribution because the likeliest (average) value of capture for landfills in the U.S. was given by the U.S. EPA. A normal distribution was used for the raw grease transportation based off of the transportation distances determined from routes of GTW collection by RRWM from the longitudinal study (summarized in Table 4.1 in Chapter 4. Depending on scenario, the raw grease feed rate was varied uniformly between 250-10,000 gal/h for GTW and 25-1,000 gal/h for SSG. The feed rates were different for the two greases because there was a much larger volume of GTW processed because of the amount of water and solids present in the raw grease. Table 5.19 shows the raw grease feed rates and corresponding biofuel production for GTW and SSG in the cool season.

Table 5.19: Raw grease and biodiesel processing by hourly and annual rates.

		Unit	Base Case	Low	High
GTW	Hourly raw grease	gal/h	5,000	250	10,000
	Hourly biodiesel	gal/h	150	7.5	310
	Annual raw grease	MMgal/y	37	1.9	74
	Annual biodiesel	MMgal/y	0.75	0.04	1.5
SSG Cool	Hourly raw grease	gal/h	500	25	1,000
	Hourly biodiesel	gal/h	176	8.8	353
	Annual raw grease	MMgal/y	3.7	0.19	7.4
	Annual biodiesel	MMgal/y	0.87	0.04	1.7

The raw grease properties and fitted distributions are each dependent on the longitudinal study data for GTW and SSG which are discussed in the following sections.

"Predictions" is the term used for the economic and environmental values that were tracked during the sensitivity analysis. Lists of predictions for the global warming potential are shown in Table 5.20 and the economics are shown in Table 5.21.

Table 5.20: Global warming potential predictions for Monte Carlo simulation.

	Prediction		Abbreviation		Description	Unit
Biodiesel Production Process	Biofuel Production	Biodiesel utilities	BD U		GWP_{100} of biodiesel utilities	gCO_2eq/kg-RawGrease
	Biofuel Production	Avoided LSD	BD Av		GWP_{100} of low-sulfur diesel displaced by biodiesel production	gCO_2eq/kg-RawGrease
	Biofuel Production	Biodiesel with credit	BD wC		GWP_{100} of biodiesel production process including saving from avoided products/co-products (no waste treatment of solids/secondary wastewater)	gCO_2eq/kg-RawGrease
	Biofuel Production	Biodiesel w/o credit	BD woC		GWP_{100} of biodiesel production process not including saving from avoided products/co-products (no waste treatment of solids/secondary wastewater)	gCO_2eq/kg-RawGrease
Waste Dispsosal Scenarios	Biofuel Production	Anaerobic digestion with biogas upgrading	Biofuel	A CNG	GWP_{100} of grease-to-biodiesel process with wet solids disposal to anaerobic digestor and biogas upgrading to CNG	gCO_2eq/kg-RawGrease
	Biofuel Production	Anaerobic digestion with cogeneration	Biofuel	A CoG	GWP_{100} of grease-to-biodiesel process with wet solids disposal to anaerobic digestor and methane cogeneration to produce heat and electricity	gCO_2eq/kg-RawGrease
	Biofuel Production	Landfilling with no gas capture	Biofuel	L NoCap	GWP_{100} of grease-to-biodiesel process with wet solids disposal to landfill with no landfill gas collection	gCO_2eq/kg-RawGrease
	Biofuel Production	Landfilling with cogeneration of captured gas	Biofuel	L CoG	GWP_{100} of grease-to-biodiesel process with wet solids disposal to landfill and cogeneration to produce heat and electricity from collected landfill gas	gCO_2eq/kg-RawGrease
	Biofuel Production	Landfilling with flaring of caputred gas	Biofuel	L Flare	GWP_{100} of grease-to-biodiesel process with wet solids disposal to landfill and flaring of collected landfill gas	gCO_2eq/kg-RawGrease
	Biofuel Production	Incineration without heat recovery	Biofuel	I NoHR	GWP_{100} of grease-to-biodiesel process with wet solids disposal to incinerator without heat recovery	gCO_2eq/kg-RawGrease
	Biofuel Production	Incineration with heat recovery	Biofuel	I HR	GWP_{100} of grease-to-biodiesel process with wet solids disposal to incinerator with heat recovery	gCO_2eq/kg-RawGrease
	Business as Usual	Anaerobic digestion with biogas upgrading	As Usual	A CNG	GWP_{100} of raw grease wet solids (including lipids) disposal to anaerobic digester and methane upgrading to CNG	gCO_2eq/kg-RawGrease
	Business as Usual	Anaerobic digestion with cogeneration	As Usual	A CoG	GWP_{100} of raw grease wet solids (including lipids) disposal to anaerobic digestor and methane cogeneration to produce heat and electricity	gCO_2eq/kg-RawGrease
	Business as Usual	Landfilling with no gas capture	As Usual	L NoCap	GWP_{100} of raw grease wet solids (including lipids) disposal to landfill with no landfill gas collection	gCO_2eq/kg-RawGrease
	Business as Usual	Landfilling with cogeneration of captured gas	As Usual	L CoG	GWP_{100} of raw grease wet solids (including lipids) disposal to landfill and cogeneration to produce heat and electricity from collected landfill gas	gCO_2eq/kg-RawGrease
	Business as Usual	Landfilling with flaring of caputred gas	As Usual	L Flare	GWP_{100} of raw grease wet solids (including lipids) disposal to landfill and flaring of collected landfill gas	gCO_2eq/kg-RawGrease
	Business as Usual	Incineration without heat recovery	As Usual	I NoHR	GWP_{100} of raw grease wet solids (including lipids) disposal to incinerator without heat recovery	gCO_2eq/kg-RawGrease
	Business as Usual	Incineration with heat recovery	As Usual	I HR	GWP_{100} of raw grease wet solids (including lipids) disposal to incinerator with heat recovery	gCO_2eq/kg-RawGrease

Table 5.21: Economic predictions for Monte Carlo simulations.

Prediction	Abbreviation	Unit	Description
Cost of raw materials	CRM	$/y	Cost of raw materials for biodiesel production
Cost of utilities	CUT	$/y	Cost of heat, electricity, and hot oil
Cost of waste treatment	CWT	$/y	Cost of disposal of waste solids, wastewater, and biodiesel production
Revenue from sales	RFS	$/y	Revenue from sales
Cash flow	CF	$/y	Annual cash flow
Fixed capital investment	FCIL	$	Fixed capital investment for equipment
Simple payback	PB	y	payback period (FCIL/CF)
Biodiesel production	BD Prod	gal/y	Amount of biodiesel produced per year

5.4.1. Data Fitting

For GTW, the special tank in the longitudinal study was 500 gal representing approximately one truck load of raw grease collected from interior grease traps. The longitudinal study showed that there was a large variability in the lipid content and floating solid volume of the waste. To analyze the effect of accumulation of GTW, three different grease content distributions were studied. First the unaltered longitudinal study data was used (distribution A1). Using Oracle Crystal Ball, the longitudinal study data was fit to distributions and Monte Carlo was run for 10,000 trials to randomly assign values to the float grease volume, sediment volume, lipid mass in the floating layer, and FFA mass in the lipids. This was repeated five times for a total of 50,000 randomly chosen values for the composition assumptions. For each 10,000 trial run, two new data sets were created: (1) average of every 10 values (A10) and (2) average of every 100

values (A100). New distributions were then set to the data sets of A10 and A100 variables to represent aggregation of raw grease.

Unlike GTW, the SSG longitudinal data was determined from aggregated samples of SSG; therefore the distributions based off of the longitudinal study were adequate for estimates of accumulated SSG. However, due to the correlation of temperature to lipid content, the longitudinal study data was split into three temperature zones and Oracle Crystal Ball was used to fit a distribution to each of the temperature data sets.

The longitudinal study data was fit to a distribution and Monte Carlo was used to randomly choose 10,000 data points along the distribution 5 different times. For each trial, a box plot of the fitted distribution was compared to a box plot of longitudinal study data shown in Figure 5.8.

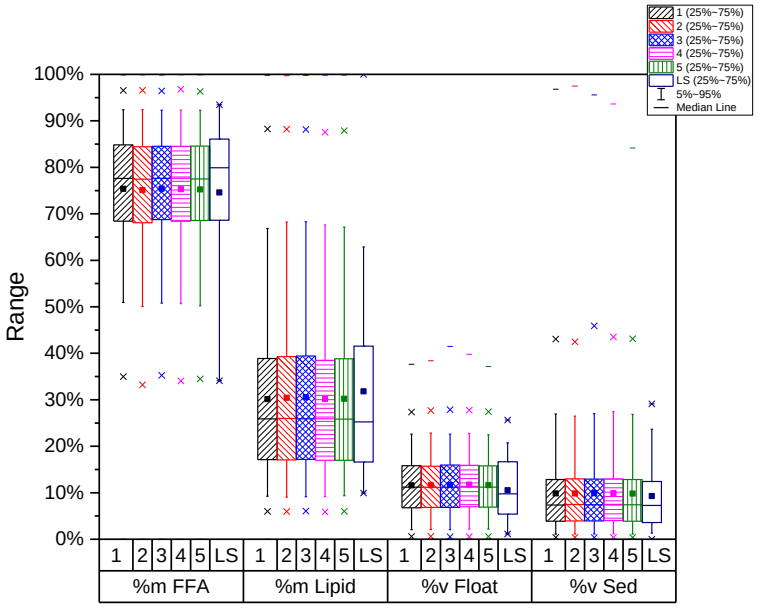


Figure 5.8: Repeatability of simulations for raw GTW compared to longitudinal study (LS). 1-5 represent trials of 10,000 randomly chosen values over the fitted distribution. Boxes represent 25-75 percentiles, whiskers represent the 5-95 percentiles, x represents 1-99 percentiles, - represents minimum and maximum, the middle line represents the median, and the filled square represents the mean.

The five trials compared to the longitudinal study data were similar and showed that the chosen distributions provided a good representation of the data from the longitudinal study. This assumption was based off of comparing the mean (filled squares), median, and 25-75 percentile boxes of the trials to the longitudinal study data. For the repeatability, the 5-95 percentiles (whiskers) were all consistent between the five trials. The %mFFA 5 percentile whisker was 50 %mFFA for the fitted data compared to 35 %mFFA for the longitudinal study data. There were only two cases of lower FFA content in the longitudinal study data compared to the fourteen other data points above 60 %mFFA.

The longitudinal study data for each season was fit to a distribution. Each of the fitted distributions was run using Monte Carlo for 10,000 trials. The fitted data was plot using a box plot and compared to a box plot of the longitudinal study shown in Figure 5.9. The percent mass of the FFA, percent mass of lipids, and percent mass of wet solids were all analyzed. In each season, the box and whisker plots of the fitted data were comparable to the longitudinal study data. For the cool distributions, the fitted data is similar to the longitudinal study data. The boxes, whiskers, medians, and means are all similar between the data sets. The lower whisker (5 percentile) is slightly higher for the fitted data (60%) compared to the longitudinal data (40%). This is similar to GTW where there was one low FFA content compared to 16 other data points above 60 %mFFA. In the temperate distributions, the boxes, whiskers, means, and medians are all similar for the variables.

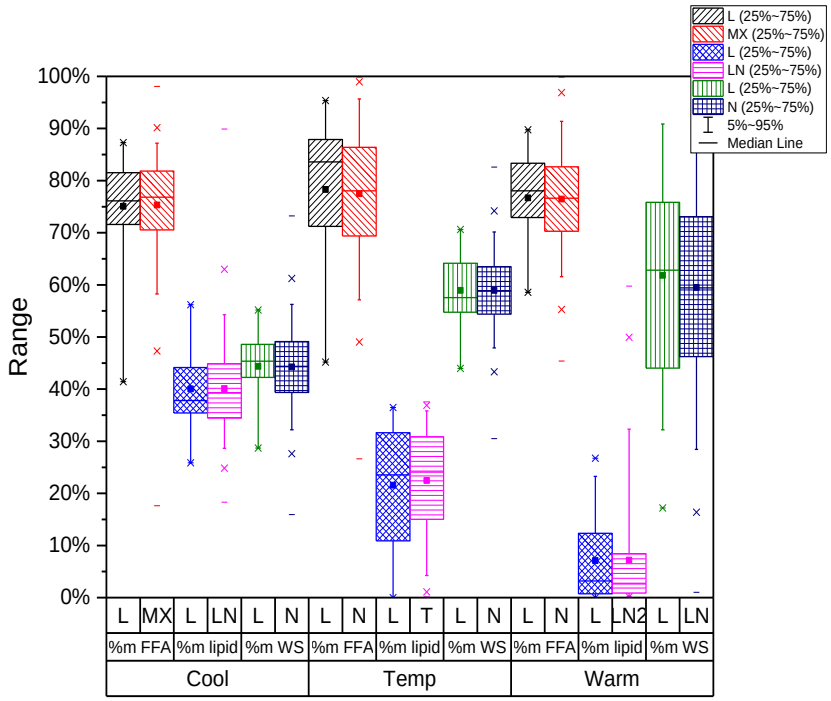


Figure 5.9: SSG fitted distributions for %m FFA, %m lipid and %m wet solids compared to longitudinal study data (L) and categorized by seasonal variability. MX = minimum extreme, LN = lognormal, T = triangular, N = normal. Boxes represent 25-75 percentiles, whiskers represent the 5-95 percentiles, x represents 1-99 percentiles, - represents minimum and maximum, the middle line represents the median, and the filled square represents the mean.

The lower whiskers (5 percentiles) were slightly higher for the fitted data than for the longitudinal study data. The longitudinal data was small so in the low number of occurrences of lower %m lipids or %m FFA that could be outliers skews the longitudinal study data percentiles to be lower. Since the occurrences were low, when the Monte Carlo was used for the fitted data, the low values did not occur as often which was why the 5 percentile was higher in the fitted data compared to the longitudinal data. In the warm season, %mFFA and %mWS fit well to the longitudinal study data. There was a slight discrepancy in %m lipid for the longitudinal study data compared fitted data for the 95 percentile range. The standard deviation was 108% which permits for higher

lipid contents to be possible; while all of the other data sets were truncated between 0.15% and 99.9%, the %m lipids in this case was truncated to 60%. It is highly improbable that anything above 60% lipids would occur during the warm months; this occurrence is rare for the cold season so it most likely would not occur in the warm season.

5.4.2. Environmental Impacts Sensitivity Analysis

5.4.2.1. 100-Year Global Warming Potential of Biofuel Production from Grease Trap Waste

The GWP_{100} of the biofuel production process was determined for each of the distribution sets for GTW (Figure 5-9). The results do not show the waste management of the secondary wastewater or the disposal of the waste solids. The A1 distribution represented one truck of 500 gal of GTW (distribution fit to the longitudinal study data), the A10 distribution represented the average of ten trucks of GTW, and the A100 represented the average of 100 trucks of GTW. Within each distribution, three plant capacity scenarios were studied: (1) an unfixed plant capacity with variable flow rate (UV), (2) a fixed plant capacity of 5,000 gal/h and variable flow rate (FV), and (3) a fixed plant capacity of 5,000 gal/h and fixed flow rate of 5,000 gal/h (F5). The left half of Figure 5.10 compares the results between the total GWP_{100} with and without the credit of biofuel production. The credit refers to the low-sulfur diesel and heavy fuel oil avoided with biodiesel and biobunker production. The right side of Figure 5.10 compares the GWP_{100} associated with two sub-processes of the biofuel production: (1) The avoided LSD and (2) the utilities used in the biofuel production.

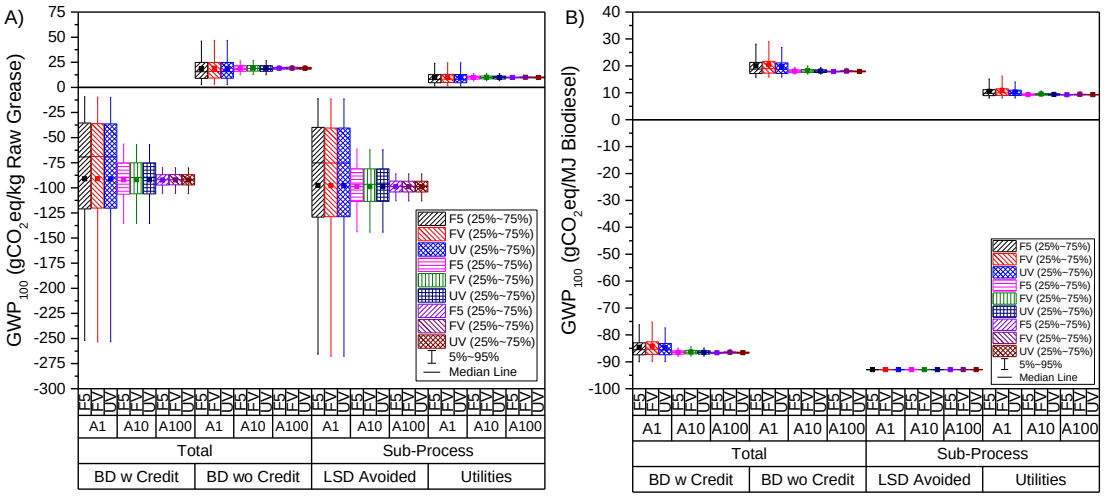


Figure 5.10: Global warming potential of biodiesel production from GTW. (A) GWP_{100} in g CO_2eq/kg Raw Grease and (B) GWP_{100} in g CO_2eq/MJ Biodiesel. Scenarios include longitudinal study data (A1) and concentrated GTW (A10 and A100). Plant variability included unfixed plant size with variable feed rate (UV), fixed plant size with variable feed rate (FV), and fixed plant size with fixed 5,000 gal/h feed rate (F5). Boxes represent 25-75 percentiles and whiskers represent 5-95 percentiles. The filled box represents the average and the interior horizontal line represents the median.

For all GWP_{100} studied, the averages were similar between the distribution that was used (A1, A10, A100). The ranges became smaller with each distribution because the A1 variability of the composition of raw GTW was large; once every ten trucks were averaged, the variability decreased, and when 100 trucks were averaged, the variability was small. The capacity of the plant had little effect on the GWP_{100} between the three scenarios studied because the functional unit was chosen as per kg of Raw GTW. The GWP_{100} was normalized by the amount of raw grease fed into the plant so as the feed rate varied, the GWP_{100} scaled with the flow rates. The GWP_{100} of biofuel production with credit was always lower than zero regardless of raw grease composition.

Figure 5.10 displays the GWP_{100} impacts of the biofuel production as a function of 1 MJ of biodiesel produced. In all of the scenarios analyzed, the GWP_{100} impacts of

biofuel production without credit was approximately between 20-35 g CO_2eq/MJ Biodiesel. The GWP_{100} impact of LSD production and combustion is 93 g CO_2eq/MJ Biodiesel. Soybean biodiesel has a GWP_{100} of 32 g CO_2eq/MJ Biodiesel. Not including the credit or the waste treatment, the biofuel production process had a lower GWP_{100} than LSD and is comparable to soybean biodiesel.

In the sub-processes for the left graph, the utilities were shown to be the largest contributor toward the positive GWP_{100}. The utilities account for approximately 70% of total positive GWP_{100}. The natural gas needed for steam was the highest impact utility in the biofuel production. Steam was needed for the brown grease lipid separation, FAME conversion, and FAME purification. The avoided LSD was the process that contributed the most credit to the biofuel production. LSD accounted for about 80% of the avoided emissions. The GWP_{100} of bunker was high, but there was much less biobunker produced compared to the biodiesel. When the functional unit was a MJ of biodiesel, there was no variability in the avoided LSD because the amount of fuel remained the same.

Because the plant capacity scenarios did not show variability in GWP_{100} results, the disposal scenario study was performed on only the fixed plant size, variable feed rate scenario (FV) for all distributions. Figure 5.11 shows the GTW GWP_{100} for business as usual compared to that of the biofuel production for the multiple solid waste disposal options.

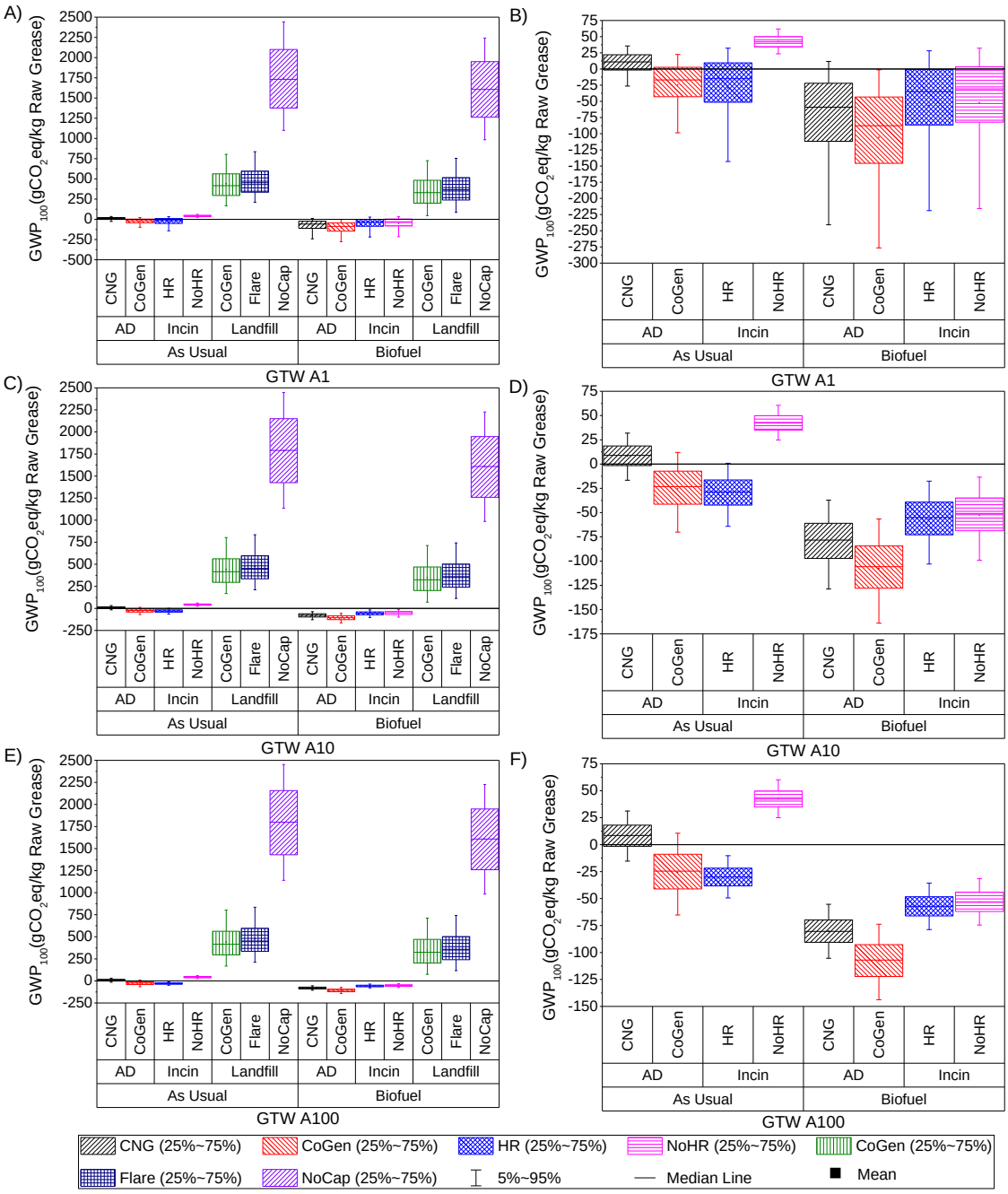


Figure 5.11: Comparison of business as usual to biofuel production from GTW for various biosolids disposal scenarios. (A) and (B) represent the A1 distribution of the longitudinal study data, (C) and (D) represent the A10 accumulation of GTW, and (E) and (F) represent A100 accumulation of GTW. Anaerobic digestion (AD) with biogas upgrading to CNG (CNG) and cogeneration of heat and electricity (CoG); incineration (Incin) without heat recovery (No) and with heat recovery (HR); and landfilling (Landfill) with cogeneration of heat and electricity from captured landfill gas (CoG), flaring of captured landfill gas (F), and uncaptured landfill gas (No). The first column shows all of the waste scenarios while the right column omits landfilling.

The landfill scenario for both biofuel production and business as usual has the highest GWP_{100} with the no gas capture option as the largest value. The high GWP_{100} is because of the large amount of methane that is emitted to the atmosphere in this scenario. Even with cogeneration of heat and electricity, there is not enough avoided natural gas or electricity to produce a negative GWP_{100}. In all dispsosal scenarios, except the incineration with heat recovery, the GWP_{100} for biofuel production is lower than that of the business as usual. The lower GWP_{100} is due to the GWP_{100} credit for the avoided LSD. The results are similar to the base case. Also, the trends are all the same regardless of distribution; the only differences is the narrowing of the whiskers as more data is aggregated together. For the biofuel production scenarios, the feed rate, lipid content, and float volume are all the most important variables that have the greatest sensitivity to the GWP_{100} results.

5.4.2.2. 100-Year Global Warming Potential of Biofuel Production from Sewage Scum Grease

The GWP_{100} of the biofuel production process for SSG over the three seasonal distributions was determined; Figure 5.12 displays the results of the Monte Carlo simulation on a per kg raw grease and per MJ biodiesel basis. The GWP_{100} does not include waste management of the SSG solids or wastewater.

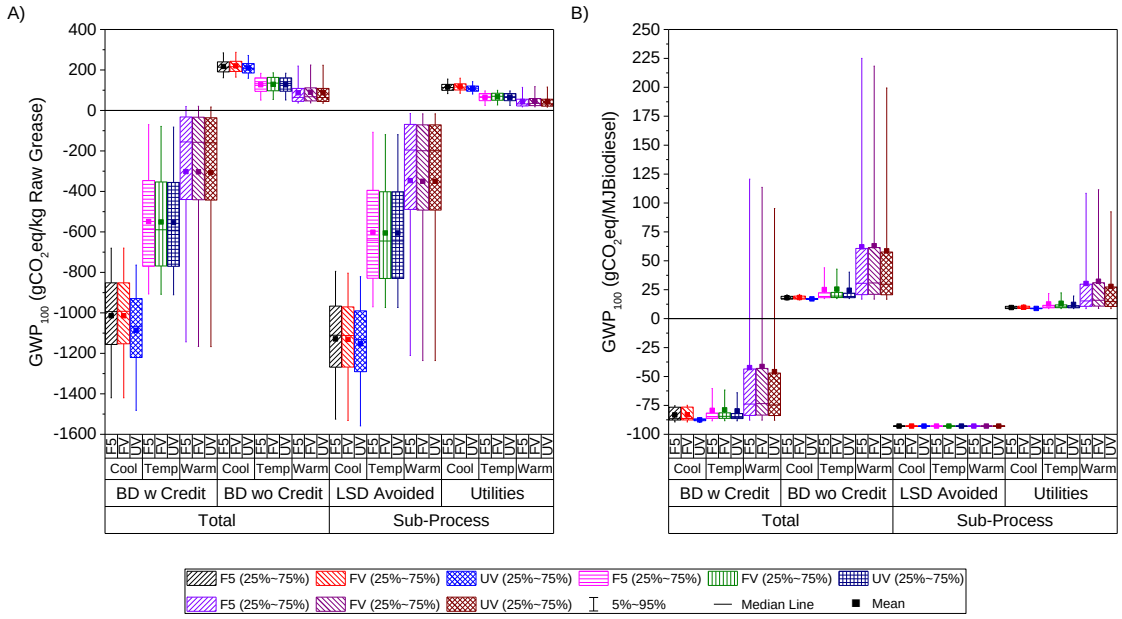


Figure 5.12: Global warming potential of biofuel production from SSG. (A) GWP_{100} in g CO_2eq/kg Raw Grease and (B) GWP_{100} in g CO_2eq/MJ Biodiesel. Scenarios include longitudinal study data for three seasons: cool, temperate, and warm. Plant variability included unfixed plant size with variable feed rate (UV), fixed plant size with variable feed rate (FV), and fixed plant size with fixed 500 gal/h feed rate (F5). Boxes represent 25-75 percentiles and whiskers represent 5-95 percentiles. The filled box represents the average and the interior horizontal line represents the median.

The utilities used for biofuel production were the largest contributor to the GWP_{100}, while the avoided LSD accounted for the negative GWP_{100} for total biofuel production including the credit. When the functional unit was per kg raw grease, the warm temperature had the lowest positive GWP_{100} (used the least amount of utilities compared to the cool and temperate seasons). However, the warm season had less biodiesel produced so the avoided LSD had the highest GWP_{100} compared to the cool and temperate seasons. The GWP_{100} biofuel with credit value in the warm season was sometimes positive which showed that there was such a small amount of biodiesel produced that the avoided LSD credit was not enough to net to a negative GWP_{100} value.

When the functional unit was per MJ of biodiesel, the biofuel production in the warm season was low which caused the GWP_{100} to be high. Between all of the plant capacity scenarios (UV, FV, and F5) in each season, all of the averages were similar and there was little variability between the 5-95 percentiles. The unfixed plant variable feed rate, fixed plant variable feed rate, and fixed plant and fixed at 500 gal/h had little difference on the 5-95 percentile range.

Because the plant capacity scenarios did not show variability in GWP_{100} results, the disposal scenario study was performed on only the fixed plant size, variable feed rate scenario (FV) for all distributions. Figure 5.13 shows the GWP_{100} for SSG business as usual compared to that of the biofuel production for the multiple solid waste disposal options. Similar to GTW and the base case results, the landfill scenario had the worst GWP_{100} compared to the other disposal scenarios. The biofuel production for the cool and temperate seasons had negative GWP_{100} for landfill flare and cogeneration of heat and electricity which can be contributed to the credit from the avoided LSD. The GWP_{100} of the biofuel production scenario showed similar results between anaerobic digestion and incineration. The business as usual GWP_{100} of incineration with heat recovery was similar to that of biofuel production because of the LHV of the brown grease lipid incineration. In the cooler seasons, there were about 40% mass lipids in the raw grease. In the incineration with biofuel production, the separation of a large amount of lipids removed most of the energy that could be recovered in the incineration; the remaining amount of waste solids had a low heating value. The biofuel production was the most important factor to the low GWP_{100} values for this scenario.

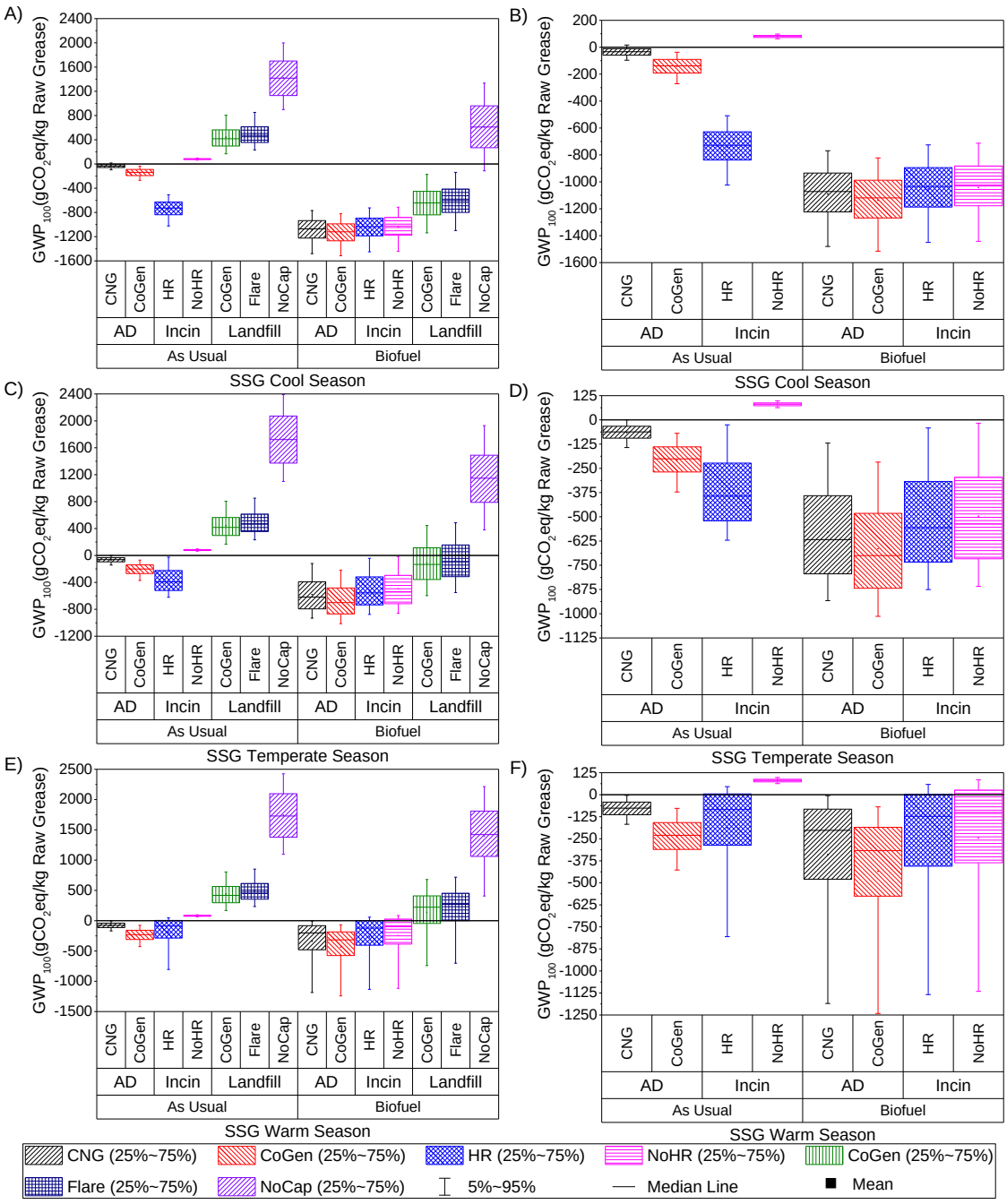


Figure 5.13: Comparison of business as usual to biofuel production from SSG in cool, temperate, and warm seasons for various biosolids disposal scenarios. Anaerobic digestion (AD) with biogas upgrading to CNG (CNG) and cogeneration of heat and electricity (CoG); incineration (Incin) without heat recovery (No) and with heat recovery (HR); and landfilling (Landfill) with cogeneration of heat and electricity from captured landfill gas (CoG), flaring of captured landfill gas (F), and uncaptured landfill gas (No). The first column shows all of the waste scenarios while the right column omits landfilling.

In the warm months, there was not as much biodiesel which was why the GWP_{100} was higher and almost positive compared to the winter and temperate seasons. The business as usual anaerobic digestion with cogeneration scenario was negative, but not as beneficial as anaerobic digestion with cogeneration and biofuel production. The incineration with heat recovery was the only business as usual scenario that was comparable to biofuel production because of the benefits of the lipids in the incinerator. In the warmer months, it may be better to not make biodiesel but incinerate the lipids to avoid natural gas production for the lowest greenhouse gas emissions.

5.4.3. Economics Sensitivity Analysis

5.4.3.1. Economics of Biofuel Production from Grease Trap Waste

While the environmental impacts appear promising for biofuel production compared to business as usual, it is important that the process is also economical. The payback period was an important metric to determine the feasibility of producing biodiesel from these waste greases. Payback period is dependent on the annual cash flow and the fixed capital investment which are shown in Figure 5.14. The fixed plant, fixed feed rate scenario (F5) represented variability of composition of feed grease (black). The fixed plant with variable feed rate (FV) represented performance of a single plant that varies due to volume and composition of grease received (red). The unfixed plant with variable feed rate (UV) represented the distribution of building many plants based on local grease volumes (blue).

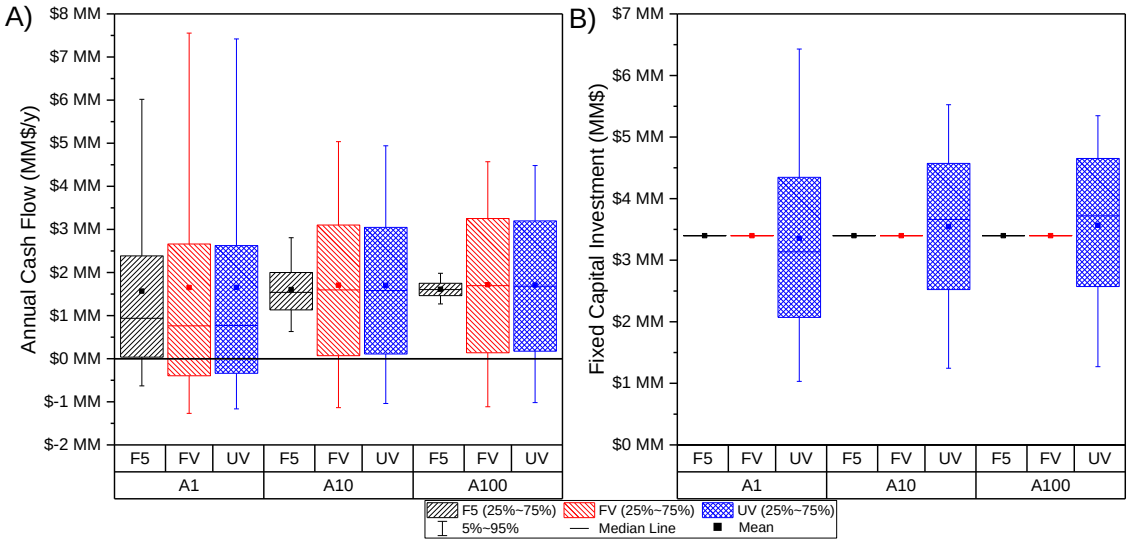


Figure 5.14: (A) annual cash flow and (B) fixed capital investment for GTW for non-aggregated GTW (A1) and aggregated GTW (A10 and A100). Plant capacity studied fixed plant size at fixed 5,000 gal/h flow rate (F5), fixed plant capacity with a variable flow rate (FV), and unfixed plant capacity with variable flow rate (UV).

The fixed capital investment had no variability for the F5 and FV scenarios which was expected because the plant size was constant and should not show any changes. The unfixed plant showed the variability due to plant equipment costs that depended on the size of the plant.

The mean annual cash flow was similar between all of the GTW scenarios. As the number of aggregated data increased, the 5 and 95 confidence intervals (whiskers) decreased. The fixed variable plant size and unfixed variable plant size had little difference in annual cash flow. The fixed plant size with fixed flow (F5) rate range decreased in the A10 and A100 distributions because the feed rate no longer had an impact on the annual cash flow; the result was only attributed to the raw grease content which with aggregation narrows the variability closer to the mean. There was a decrease in the cash flow range between the F5 A10 and F5 A100 scenarios which showed an

effect due to aggregation; this aggregation effect was not as apparent with the variable feed rate scenarios (FV and UV) because the flow rate variability counteracted the decrease in composition variability with aggregation. The A1 data also had the most chances of producing a negative cash flow.

An analysis was performed to see at what float volume/lipid content and feed rates payback period would be negative or take a long time. Figure 5.15 is a plot of the effect of lipid content/float volume and the feed rate on the economic feasibility of biofuel production. The economic feasibility is represented by situations where the cash flow is positive and the payback period is less than 5 y (green x). As the raw grease is concentrated (A10 and A100), the trend line appears to remain the same. In each aggregation scenario, the regions are approximately the same; however, the range in lipid content is decreased due to less variability in the feedstock. Ideal operation of a biofuel plant would be in the green area which shows a minimum flow rate of 2,000 gal/h and lipid*float content of 5% to be economically feasible. When economic feasibility is possible, the amount of biodiesel produced has enough revenue to overcome the cost of manufacturing. The amount of biodiesel produced is dependent on the amount of brown grease which is affected by the raw grease composition and feed rate.

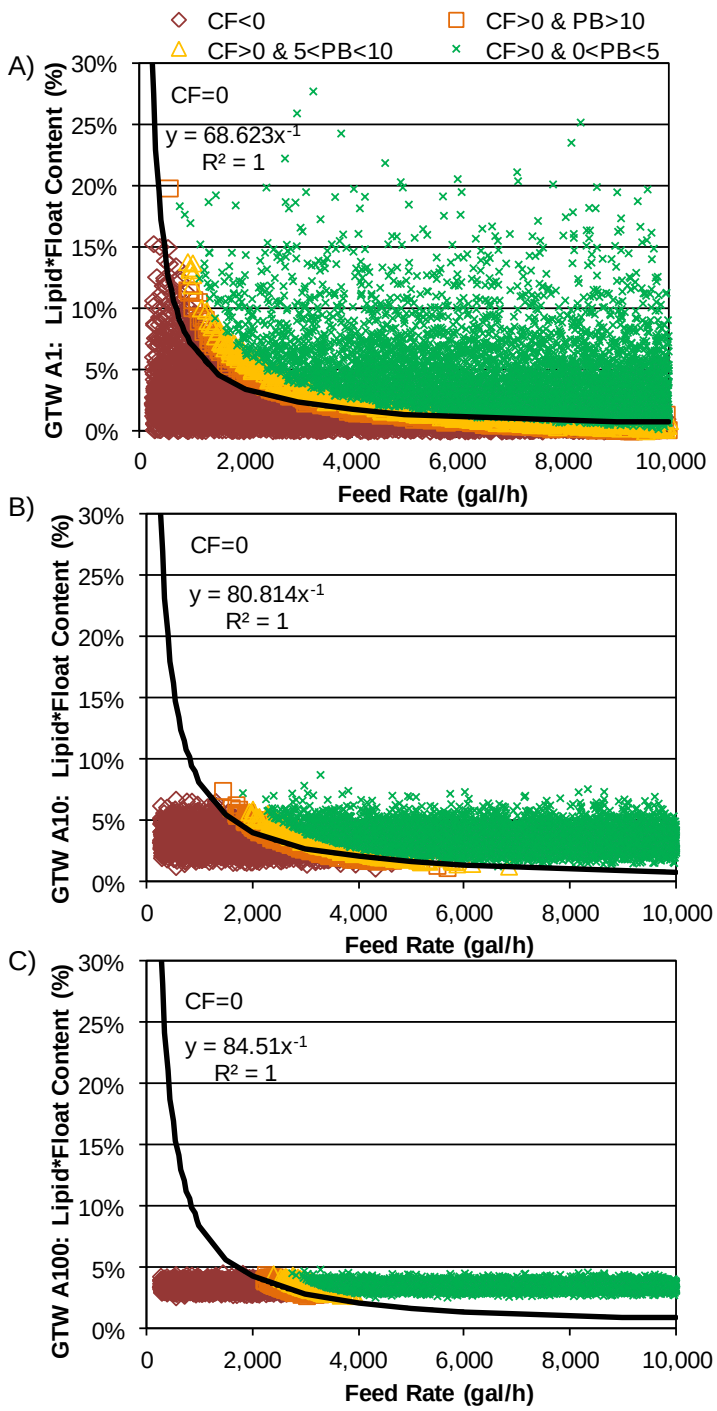


Figure 5.15: Map of economic sensitivity of GTW Raw Grease composition and feed rate. Distributions used: (A) GTW A1, (B) GTW A10, and (C) GTW A100. Economic conditions studied: negative cash flow (red diamond), positive cash flow with payback period greater than 10 y (orange square), positive cash flow with payback period between 5 and 10 y (yellow triangle), and positive cash flow with payback period less than 5 y (green x). Black line represents simplified equation where cash flow is zero.

The boundary separating regions between positive and negative cash flow is a hyperbolic equation represented by the black line. This line was estimated by using Microsoft Excel to determine the slope and intercept of lipid*float content (y) and feed rate (x). The negative of the intercept divided by the slope gives the constant in the power equation shown in Figure 5.15. The parameters used in the equation are shown in Table 5.22.

Table 5.22: GTW fitted equation parameters to estimate cash flow.

	Slope	Intercept	Constant (Intercept/Slope)
A1	14885	-1021425	68.623
A10	16867	-1363086	80.814
A100	17512	-1479975	84.510

5.4.3.2. Economics of Biofuel Production from Sewage Scum Grease

The payback period was also determined for SSG data for each seasonal variability distribution set. The annual cash flow and fixed capital investment are shown in Figure 5.16.

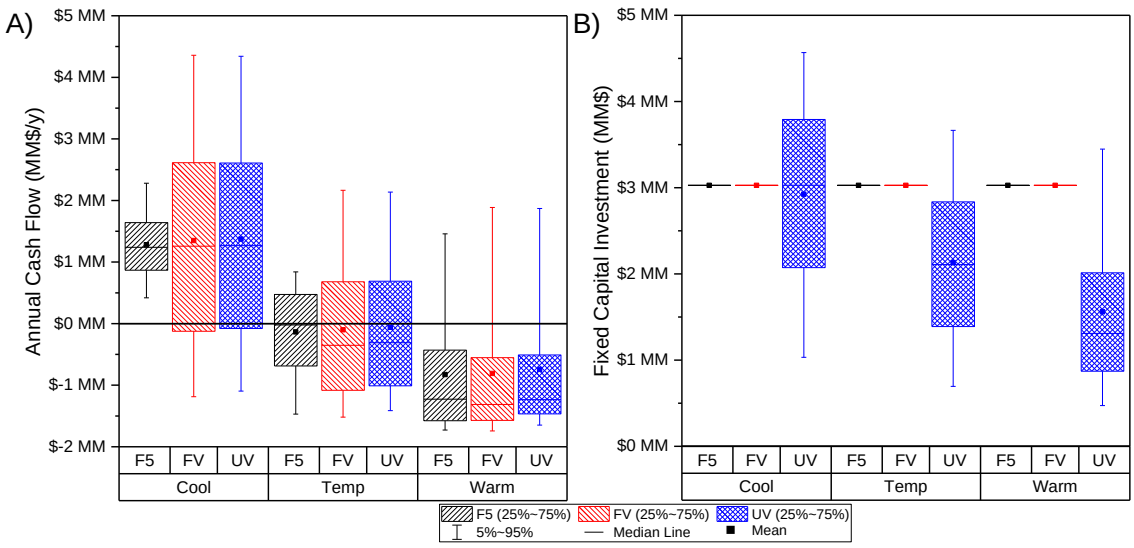


Figure 5.16: (A) annual cash flow and (B) fixed capital investment for SSG during cool, temperate (temp), and warm (warm) seasons. Plant capacity studied fixed plant size at fixed 500 gal/h flow rate (F5), fixed plant capacity with a variable flow rate (FV), and unfixed plant capacity with variable flow rate (UV).

The cool weather distribution had very few occurrences where annual cash flow was less than zero. The temperate months had annual cash flow less than zero about half all trials, and the warm months had the entire 25-75 percentile box less than zero. The fixed capital investment for the warm months was lowest for the unfixed variable scenario because the size of the equipment was smaller because of the lower amount of biodiesel that was produced.

Figure 5.17 is a plot of the effect of lipid content/float volume and the feed rate on the economic feasibility of biofuel production. The economic feasibility is represented by situations where the cash flow is positive and the payback period is less than 5 y (green x).

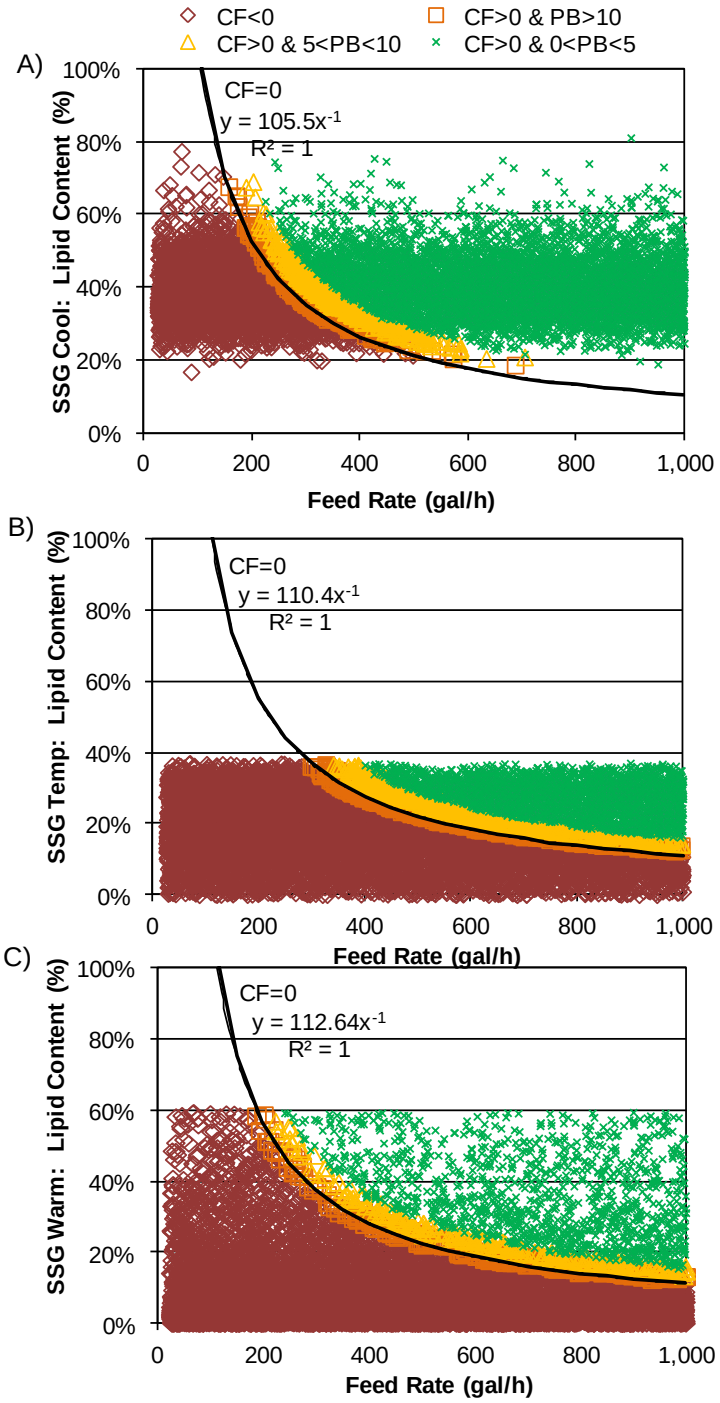


Figure 5.17: Map of economic sensitivity for SSG raw grease composition and feed rate. Distributions based on SSG seasonal data: (A) cool, (B) temperate, and (C) warm. Economic conditions studied: negative cash flow (red diamond), positive cash flow with payback period greater than 10 y (orange square), positive cash flow with payback period between 5 and 10 y (yellow triangle), and positive cash flow with payback period less than 5 y (green x). Black line represents simplified equation where cash flow is zero.

In the warm season, the lipid content needed to be above 20% and 1,000 gal/h or 300 gal/h and around 60% lipid content. In the temperate months, the same trend was shown as the warm weather; however, it had slightly more occurrences of higher brown grease lipid contents in the temperate months than in the warm months. The winter season had the most occurrences of high lipid contents and showed good economic return for feed rates above 600 gal/h.

The boundary separating regions between positive and negative cash flow is a hyperbolic equation represented by the black line. This line was estimated by using Microsoft Excel to determine the slope and intercept of lipid*float content (y) and feed rate (x). The negative of the intercept divided by the slope gives the constant in the power equation shown in Figure 5.17. The parameters used in the equation are shown in Table 5.23.

Table 5.23: SSG fitted equation parameters to estimate cash flow.

	Slope	Intercept	Constant (Intercept/Slope)
Cool	14182	-1496126	105.5
Temperate	14129	-1559852	110.4
Warm	14464	-1629268	112.6

5.5. Conclusions

For both SSG and GTW, the economic feasibility of the process depended strongly upon the total volume of biodiesel produced. The amount of biodiesel produced scaled with the amount of raw wastewater grease fed to the process and the lipid content of the raw wastewater grease. The lipid content of GTW fed to the process was 5% and

the feed rate was 1,000 gal/h then the cash flow was negative (not economically feasible), but if the feed rate was 2,000 gal/h the payback time was between 5-10 y, and if the feed rate was 4,000 gal/h the payback time was less than 5 y. Similarly for SSG, a lipid content of 30% and feed rate of 400 gal/h produced payback time of about 10 y, but if the flow rate increased to 600 gal/h the payback time was less than 5 y. The complexity of biodiesel from SSG was also increased due to the seasonal variability of lipid content. Much like a harvested crop, SSG-only feedstock may only be feasible at certain seasons thereby requiring accumulation of SSG to meet necessary feed rates. However, if SSG was stored, it would degrade over time and, therefore, it may be more beneficial to co-digest with sewage sludge for anaerobic digestion if the WRRF has this technology. Therefore, utilizing SSG as part of the brown grease supply chain in a GTW biofuel production process may be the most beneficial option for biofuel production from wastewater greases. Obtaining a reliable supply of GTW and/or SSG with lipid content as high as possible is critical for implementing economically-viable wastewater grease to biofuel process. The economic feasibility may require establishing a centralized biofuel production facility and transporting GTW and SSG from other metropolitan regions to ensure that there is enough feedstock for economic biofuel production.

The environmental impact section showed that biofuel production and anaerobic digestion of biosolids with cogeneration of heat and power has the lowest net environmental impact. For cases where biofuel production is not economical or feasible, and business as usual is employed, the incineration with heat recovery is the best environmental option followed by either anaerobic digestion option.

The results presented in the chapter are in partial fulfillment of the WERF grant and have been reported for peer-review (Cairncross et al., 2015). A policy paper is also in preparation for submission to Environmental Science and Technology (Hums, Olson, et al., 2016).

Chapter 6. Conclusions

6.1. Summary

Wastewater greases are stored energy that are currently un-utilized in the food and wastewater system, but could be recaptured and converted to biodiesel which is a value-added product that has high demand in today's economy and policies towards reducing greenhouse gas emissions. The goal of this work was to analyze the environmental impacts of biodiesel produced from wastewater greases. These wastewater greases are currently disposed of through land application, landfills, anaerobic digestion, or incineration. Brown grease diversion from solid waste for biodiesel production provides a high-value, low-carbon product that can displace petroleum diesel. While the technical conversion of biodiesel from wastewater greases is not novel, the research presented in this thesis incorporates the variability of wastewater grease composition, technical challenges in producing biodiesel, techno-economic analysis, and life cycle assessment to provide a new investigation into the economic feasibility of commercial scale biodiesel production while maintain low greenhouse gas emissions.

Production of biodiesel from wastewater greases was shown to be technically feasible. The biodiesel produced from wastewater greases routinely met most ASTM D5761 specifications except for sulfur content, oxidation stability, and total acid number (TAN). A base wash can be used to lower the TAN and an antioxidant can be added to stabilize the fuel; however, there is no simple method to reduce the sulfur content to meet specifications. The research presented in Chapter 3 showed that vacuum distillation had effectiveness at reducing the sulfur content by 75-96% from brown grease to distillate FAME with consistent distillate sulfur content around 30 ppm S. In the Vigreaux

distillation, sulfur reduction showed an almost parabolic sulfur-temperature relationship; first distillate had high sulfur content (~200 ppm S for GTW), middle distillate had low sulfur content (~15 ppm S for GTW), and last distillate had high sulfur content (100 ppm S for GTW). SSG Vigreaux distillation showed similar a trend but the sulfur concentrations were higher than those of GTW (Figure 3.16).

The longitudinal study offered insight into the statistical variability of wastewater greases through consistent sampling over a year-long period which had not previously been performed. This study analyzed many variables in the wastewater greases including brown grease lipid content and wastewater quality. GTW was sampled from a 500 gal tank; the tank had three defined layers with the largest being wastewater, but it also included a floating grease layer and sediments. The average amount of brown grease in raw GTW was about 4% lipids but the floating layer had an average of 30%.

Ambient separation, or dewatering, of float grease reduces the amount of material to be heated by 87% which reduces energy use for heating (e.g. natural gas) and therefore, lowers heating costs and reduces the environmental impacts. Because water is the largest fraction of GTW after ambient settling, it could be beneficial to the grease hauler to not have to collect and transport substantial amounts of wastewater that could travel though the sewage system. Separation trucks exist that are capable of pumping a grease interceptor and separating the floating layer and sediments from the wastewater. However, this would only concentrate the lipids from raw GTW (4%) to about 13% lipids because of the sediments. This scenario would require more natural gas than ambient settling that could nullify the economic (and perhaps environmental) benefits of not transporting the wastewater.

The unexpected outcome of the longitudinal study was the seasonal variability of brown grease lipid content in SSG. Lipid extraction was about 7% in the warm seasons and 40% in the cool seasons. These results showed that brown grease content has a significant correlation to collection temperature which creates design challenges if biodiesel production were to be implemented at a WRRF. The seasonal variability makes SSG similar to agricultural feedstocks because production occurs at certain times of the year. SSG could be aggregated and stored at the WRRF throughout the year with biodiesel production occurring when the brown grease volume is larger. However, when SSG production is low, anaerobic digestion may be a better alternative than storage because depending on the length of the storage, the SSG would begin to degrade and produce biogas. Instead of producing biodiesel, the WRRFs could become brown grease producers by incorporating the heated separation process and selling the brown grease to biodiesel producers. A third alternative is that SSG would serve as part of a supply chain at a centralized processing facility of brown grease that includes GTW and SSG. Because of their similarities in brown grease FFA content, simultaneous biodiesel production from GTW and SSG feedstocks could be performed.

The main challenge to the economic feasibility of biodiesel production from wastewater greases is the quantity of raw grease that is processed and lipid content of the raw grease (essentially the amount of brown grease) available for conversion. Chapter 5 showed that the SSG feed rate of 3.9 MMgal/y (600 gal/h) at all lipid contents was needed to be economically feasible (Figure 5.17). However, PWD produces 0.34 MMgal/y of SSG which is not nearly enough raw grease available for economic biodiesel production. The GTW showed that a feed rate of 15 MMgal/y (4,000 gal/h) at all lipid

contents was needed to be economically feasible. These requirements can be met by GTW collectors; this feed rate has been estimated by the Delaware County Regional Water Authority (DELCORA).

The lipid content and feed rate of raw grease were also important in the environmental impact analysis. The sensitivity analysis in Chapter 4 and Chapter 5 showed that low feed rates and lipid composition contained a smaller amount of brown grease and therefore less biodiesel and biobunker were produced, which resulted in higher environmental impacts. This trend was supported by Equation 4.11 which was discussed in Chapter 4.2.6; this equation showed that environmental impacts exponentially increased when lipid contents were less than 10%. These chapters also showed that biofuel production had lower environmental impacts than current wastewater grease disposal practices because of the credits from avoiding petroleum fuels.

The disposal scenario analysis in Chapter 5 showed that the best scenario for both GTW and SSG disposal is biofuel production with biosolids disposal at an anaerobic digester. However, if biofuel production is not economically feasible because of an insufficient amount of brown grease, then disposal of the raw grease (including brown grease) to an incinerator that has heat recovery would have the lowest greenhouse gas emissions compared to landfilling or anaerobic digestion. The incineration with heat recovery is fairly similar to the biofuel option because the brown grease lipids that are sent to the incinerator have an energy content of about 37 MJ/kg; therefore, there is a significant amount of heat available for recovery if the heat recovery option is available.

6.2. Potential Domestic Biodiesel Production from Wastewater Greases

The annual domestic production of both GTW and SSG is difficult to estimate; the data collected in the longitudinal study from PWD and RRWM presented in this thesis are from a small portion of the Philadelphia region. There is a data gap between the amount of wastewater grease collected and the area in which it is collected (the capture radius); this information is needed to estimate raw grease collection on a population basis. For example, Wiltsee estimated GTW production at 16 lb/y/person.

The collection rate is not as difficult to estimate for SSG. PWD operates three WRRFs that provide wastewater treatment service for Philadelphia County plus a small amount of neighboring counties; according to PWD reports, the PWD WRRFs serve approximately 2.2 million people (PWD, 2016). PWD estimated about 1,400 ton (~341,000 gal) of SSG were generated annually, which is a rate of approximately 0.16 gal/person/y.

A population based GTW production rate is more difficult to estimate from data in the longitudinal study. RRWM collects GTW from the NJ-PA-DE tri-state area and they are not the only grease hauler in the region; the disposal practices and collection radius of these other haulers are also unknown. RRWM and some other haulers dispose of GTW at the Delaware County Regional Water Authority (DELCORA), but the nearby WRRF in Camden also accepts GTW so there is overlap in the population.

To estimate the biodiesel production, a range of collection rates reported by Wiltsee was used to estimate GTW production and 0.16 gal/person/y was used for SSG. The SSG collection rate remains the same in this analysis; however lipid contents of 21% and 41% were studied based on the seasonal variability. Wiltsee reported a GTW range of 2.05-21.78 kg/y/person with a weighted average of 8.13 kg/y/person (Wiltsee, 1998).

In this GTW analysis, it is unclear if the GTW rates provided by Wiltsee are for raw GTW (float grease, water, and sediments) or the float grease alone because collection of GTW varies by grease hauler. From the longitudinal study, raw GTW had about 4% lipid content and an estimated density of 1 kg/L while float grease had about 30% lipid content and an estimated density of 0.96 kg/L; the difference in lipid content has a large impact on the amount of biodiesel that could be produced. Therefore, the weighted average, low rate, and high rate reported by Wiltsee were used assuming both raw grease volumes and float grease volumes. Table 6.1 shows the estimated annual biodiesel production from GTW and SSG in the U.S. The analysis assumed a population of 314 million and brown grease conversion rate of 89% based on the process model in Chapter 5.

Table 6.1: Estimated U.S. annual biodiesel production from wastewater Greases.

		Raw GTW + SSG		Float GTW +SSG	
		Average	Range	Average	Range
GTW Rate	gal/p/y	2.15	0.54-5.75	2.24	0.56-5.99
GTW Raw Grease	MMgal/y	674	170-1806	702	177-1881
GTW Lipid Content	%	4%	4%	30%	30%
GTW Brown Grease	MMgal/y	24	6-65	211	53-564
SSG Rate	gal/p/y	0.16	0.16	0.16	0.16
SSG Raw Grease	MMgal/y	49	70	49	70
SSG Lipid Content	%	21%	21%-41%	21%	21%-41%
SSG Brown Grease	MMgal/y	10	10-19	10	10-19
Total Brown Grease	MMgal/y	35	16-85	221	63-584
Total Purified Biodiesel	**MMgal/y**	**31**	**15-77**	**198**	**56-524**

There is a large range of biodiesel production in these two scenarios; the average biodiesel production of the float grease scenario is 477% larger than the average of the raw GTW because of the higher amount of brown grease. In the raw GTW and SSG biodiesel production scenario, SSG is approximately 38% of average biodiesel production; however in the float grease and SSG scenario, SSG is approximately 7% of average biodiesel production. Wastewater greases have the potential to increase current biodiesel production by 1-30% for the raw grease scenario and 4-29% for the float grease scenario.

6.3. Potential Work

In the longitudinal study, there is a need for more quantitative data on the production volumes of GTW and SSG. The work by Wiltsee was performed 18 years ago and shows a large range of GTW production rates; the data are difficult to collect because each grease hauler and municipality requires different disposal methods (Wiltsee, 1998) which makes quantifying GTW difficult. Collaboration between multiple grease haulers or facilities that dispose of GTW for a longitudinal study could offer more insight into the variability of GTW on a larger scale than the 500 gal samples from interior grease interceptors used in this research. Because of the seasonal variability of SSG, it would be interesting to perform a longitudinal study across the country to see if this trend continues in warm states such as Florida and Hawaii and cool states such as Maine and Alaska. A study at five WRRF on the east coast most likely would be sufficient to analyze the seasonality. It would also be interesting to track the SSG production volumes at these facilities to get a range of SSG accumulation.

There is also an opportunity to conduct further research on the causes of the seasonal variability in SSG and its effect on biodiesel production. One hypothesis is that the sewage sludge floats to the top of the primary settling tank due to biological activity in the warmer months; however, this does not fully explain why there is not a combination floating scum and floating sludge. There is a visual difference between scum grease with and without lipids; when no lipids are present, the sludge is a dark black shiny material resembling sludge. There are also times where one week one of the WRRF has this black, sludge-like material while sampling at another WRRF the next week does not, despite the same ambient temperatures at each location. Thus, even within a season, there is an expected variation on the appearance and composition of the substrate.

The sensitivity analysis performed in this work had many different variables but the lipid content and the raw grease flow rates were the most influential parameters to biodiesel production. However, it would be interesting to analyze some of the economic parameters in the sensitivity analysis. The economic sensitivity did not include the grease disposal option in the cost of disposal; all solid wastes disposals had the same cost, but for RRWM, solid waste disposal at an anaerobic digester costs more than disposal at an incinerator.

In the second life cycle assessment in Chapter 5, only GHG emissions were explored but it would be reasonably simple to incorporate other life cycle metrics into the life cycle inventory. Examples are: energy metrics (e.g. cumulative fossil demand and renewable energy demand); criteria air emissions (e.g. carbon monoxide, particulate matter, nitrogen oxides, and sulfur oxides), and water quality metrics (e.g. acidification,

eutrophication, and ecotoxicity). The integration of these life cycle metrics into the wastewater grease process model would create a robust computational database for techno-economic analysis and life cycle impact assessment, and can be paired with Monte Carlo simulation for simultaneous sensitivity analysis.

System expansion was used to analyze the impacts associated with the co-products; however, there are alternative techniques that can be applied to co-products such as allocation methods. The co-products in system expansion displace another already occurring product; for example, biodiesel production displaces low-sulfur diesel. The displaced system is then treated as a credit or a negative value. However, in the allocation method the total impacts of the process are distributed between the product and co-products on a mass, energy, or exergy basis. For example, if in biofuel production there is 95% biodiesel and 5% biobunker on an energy basis, and the total impact were 10 g CO_2eq/MJ, then biodiesel would have an impact of 9.5 gCO_2eq/MJ. Because most of the co-products in this research are fuels, the energy or exergy allocation methods would be the most appropriate method to evaluate alternatives. These alternative allocation methods have the potential to reduce or increase the environmental impacts and offer insight into how sensitive the results are to co-product allocation.

Appendix A. Longitudinal Study

A.1. Materials and Methods

A.1.1. Development of Grease Lipid Extraction (GLE)

A series of experiments were performed on a sample of GTW (GTW sample 140611-RRWM-K-RGSEP01-T) to identify a solvent-less procedure that extracted the most lipids shown in Table A.1 with corresponding images in Figure A.1.

Table A.1: Preliminary experiments to determine lipid content in wastewater greases.

Trial	Drain	Add	Heat (60 °C)	Shake	Centrifuge	%Lipid (1,2,3)	%Solid/Water (1,2,3)
A	Y	Acid	Y	Y	Y	45,42,40	52,50,53
B	Y	Water	Y	Y	Y	40,37,32	x,48,67
C	Y	N	Y	Y	Y	39,37,37	83,53,53
D	Y	N	Y	N	Y	36,39,37	53,48,48
E	N	N	Y	Y	Y	25,31,33	64,64,61
F	N	N	Y	N	N	15,13,16	85,86,83

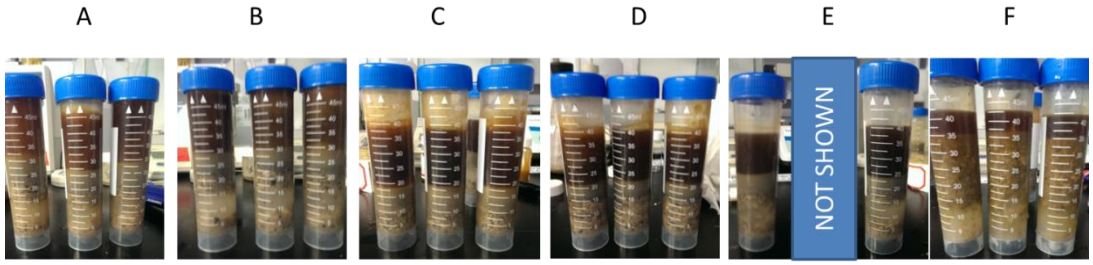


Figure A.1: Pictures of samples taken after fractionation of GTW samples corresponding to Table A.1.

From the data in Figure A.1 and Figure A.2, experiment A had the highest average lipid contents followed by B, C, and D. Samples E and F showed the lowest lipid contents. However, statistical analysis was performed to determine if the processes were significantly different from one another as shown in Figure A.2.

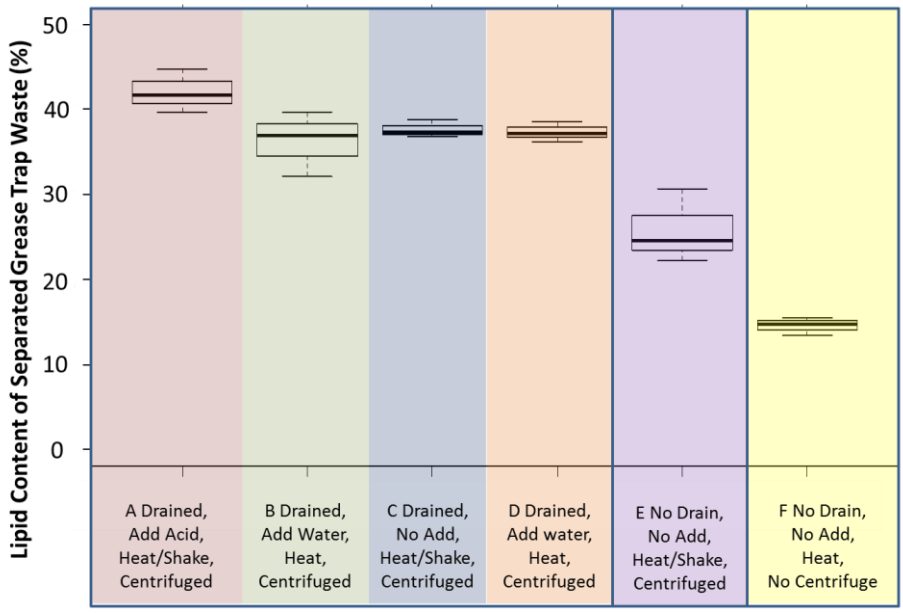


Figure A.2: Comparison of means for lipid extraction experiments.

The statistical results were similar to the observed results showing that A-D were the same, E was significantly different than A-D and F; and F was statistically different than A-D and E. These results show the importance of draining the raw grease and heating in the grease lipid extraction procedure. Adding acid also consistently showed to promote lipid extraction especially in samples of SSG (results not shown).

A.1.2. Comparison of Drexel and PWD GLE Experiments

GLE was performed by PWD and duplicates on the same sample off raw SSG were performed by Drexel University. Figure A.3 shows the results comparing the Drexel data to the PWD data.

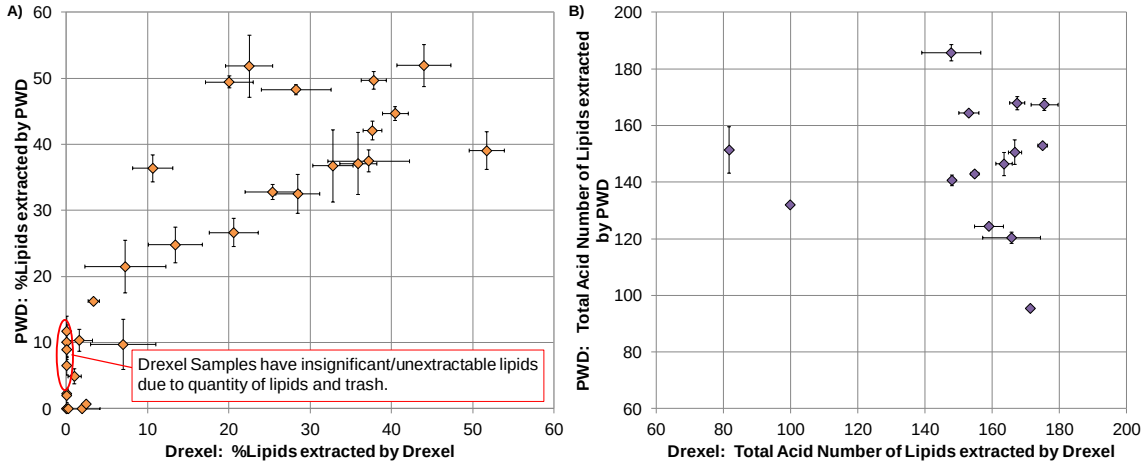


Figure A.3: Comparison between SSG lipids extracted by PWD and Drexel researchers: (A) Extractable lipid content and (B) total acid number of extractable lipids.

There was significant correlation on the 0.01 level between PWD and Drexel extractable lipids. The circled lipids in Figure A.3-A indicate Drexel samples that lipid extractions were not similar to PWD samples. No lipids were extracted from the Drexel samples compared to the roughly 7-10% lipids extracted by PWD. These were samples collected during the warmer months where there was a lot of trash in the raw sample so it was difficult for Drexel to get a non-trash sample after PWD had taken their portion for the GLE procedure.

The total acid number (TAN) of the PWD and Drexel tests were not as well correlated. The measured values of total acid number do not show strong correlation between PWD and Drexel labs and exhibit a large amount of scatter. The discrepancy could have been caused by multiple factors. The brown grease samples separated by PWD were stored for a long length of time between receiving the brown grease measuring the TAN or the brown grease was heated to melt the entire sample for a homogenous sample. Alternatively the raw SSG was stored for a length of time before

the GLE procedure by Drexel University. Finally, the discrepancy could be an indication of the inhomogeneity of SSG samples. An experiment could be performed by sampling from different locations on the same day from within the SCB tank to observe variability.

A.2. Results

A.2.1. Statistical Correlation Between Data from Grease Trap Waste Samples

The total solids in the wastewater were correlated with temperature such that total solids were lower in warmer months (Figure A.4). It is not known if this left point is an outlier, but more low-temperature samples could be taken to see if there is a correlation. This correlation was not seen in SSG total solids samples taken from the underflow water compared to temperature at sampling.

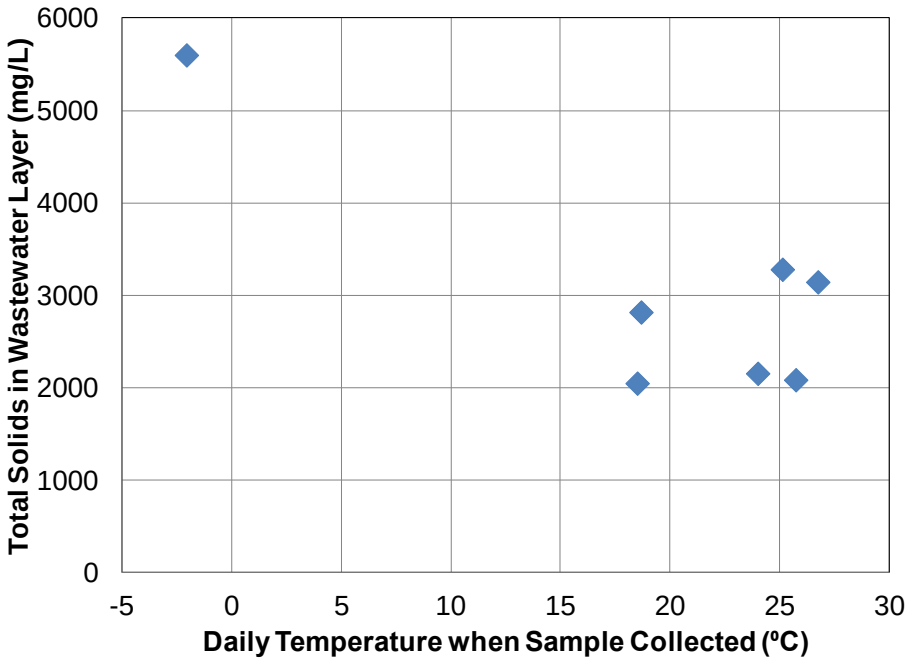


Figure A.4: Total solids in wastewater compared to temperature at sampling.

There was no correlation of total solids in the wastewater layer and float volume or sediment layer. However this correlation was seen with the chemical oxygen demand (COD) shown in Figure A.5.

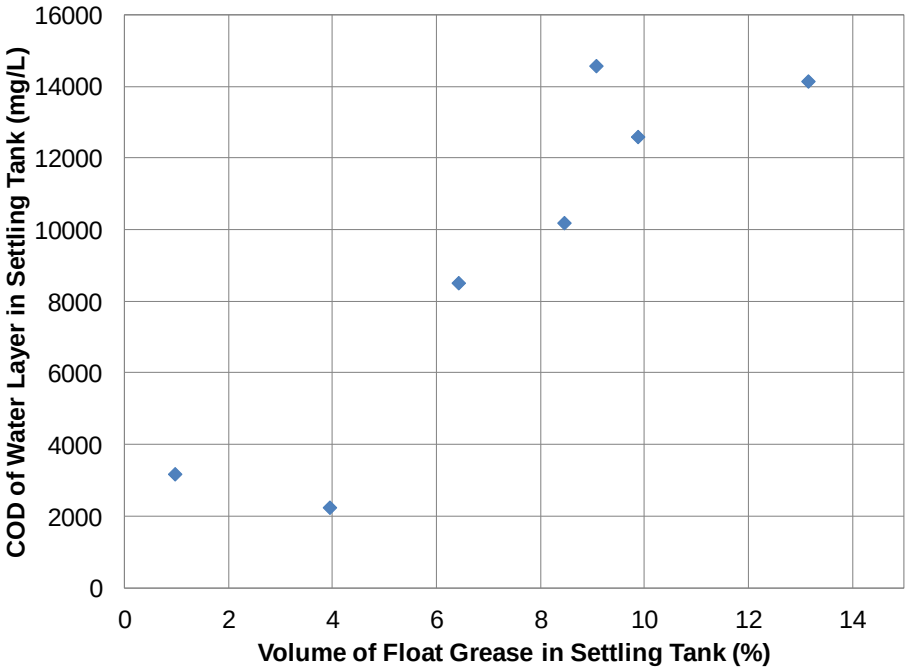


Figure A.5: Correlation between COD of settled water layer and volume of float grease in the settling tank.

The total acid number (TAN) of GTW lipids was weakly correlated to the extractable lipid content of the GTW float grease. However, as shown in Figure A.6, the majority of TAN data for GTW varied between 140-180 mg KOH/g while the lipid content varied between 15-45%. There were several outlier data points with lower TAN and/or higher lipid content that may have lead to the weak apparent correlation.

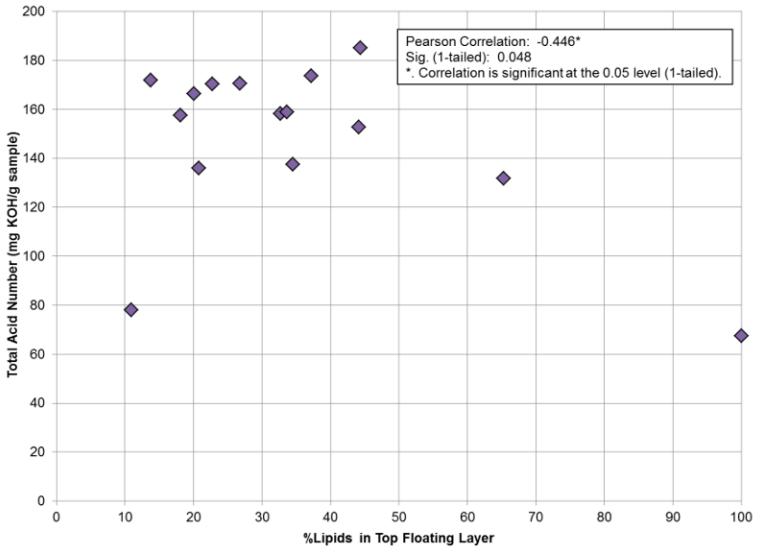
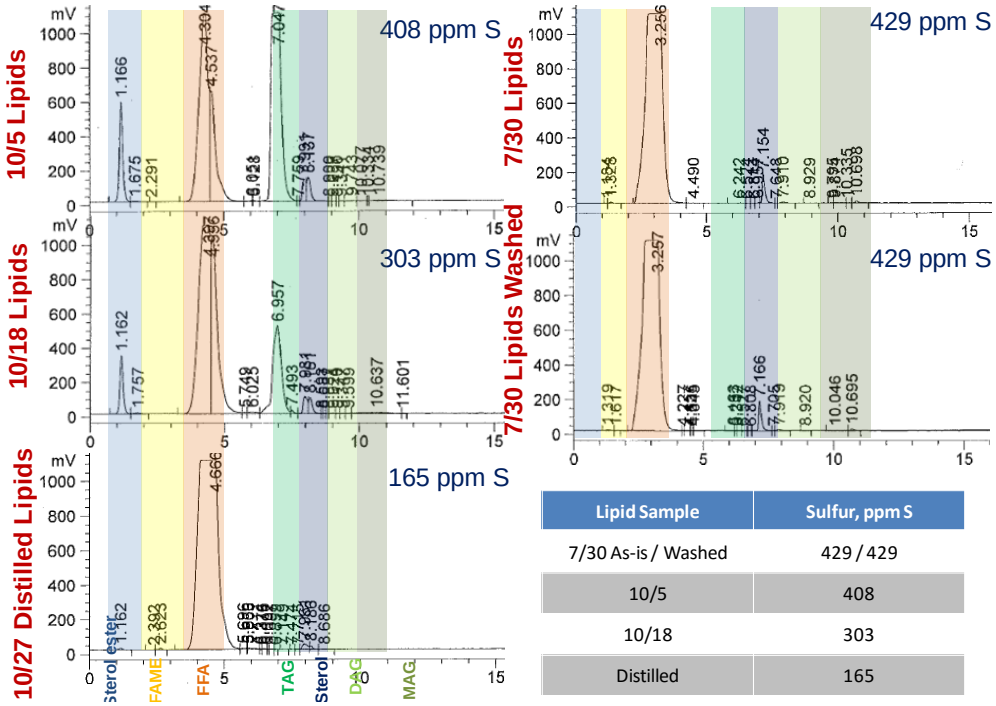


Figure A.6: Correlation between total acid number of lipids extracted from GTW and the lipid content of float grease.

Appendix B. Biodiesel Production and Sulfur Analysis

B.1. Brown Grease Pretreatment

A few experiments were performed to analyze the effects of brown grease pretreatment on sulfur content (Figure B.1).



Lipid Sample	Sulfur, ppm S
7/30 As-is / Washed	429 / 429
10/5	408
10/18	303
Distilled	165

Figure B.1: Lipid variability and pretreatment of lipids with corresponding sulfur contents.

The 10/5, 10/18, and 7/30 lipid contents all showed normal variation in brown grease sulfur contents. A portion of the 7/30 lipid contents was washed with acetic acid but showed no change in sulfur content and the HPLC data showed little change in composition. The 10/27 distilled lipids showed a lipid content of 165 ppm S and removal of the tri-acyl glycerides (TAG) peak. The removal of TAG may not be necessary because it can be converted to biodiesel through transesterification. It would be

interesting to convert both the distilled lipids and the remaining material in the bottoms to analyze differences in sulfur content. A sample of the starting lipids (prior to distillation) was not tested so sulfur reduction was unknown. If this sample is similar to other lipid contents, then there is the potential of reducing the sulfur content of brown grease FFA in half.

Two additional pretreatment experiments were performed (1) bleaching SSG brown grease lipids with acidified diatomaceous earth and (2) acidification of GTW brown grease lipids Figure B.2. The superscript 1 and 3 represent different runs of the HPLC. There was a slight difference in effluent times; however, the peaks can still be determined despite the small shift. The superscript 3 data set appears to have been overloaded which is shown by the flat top to the FFA peaks.

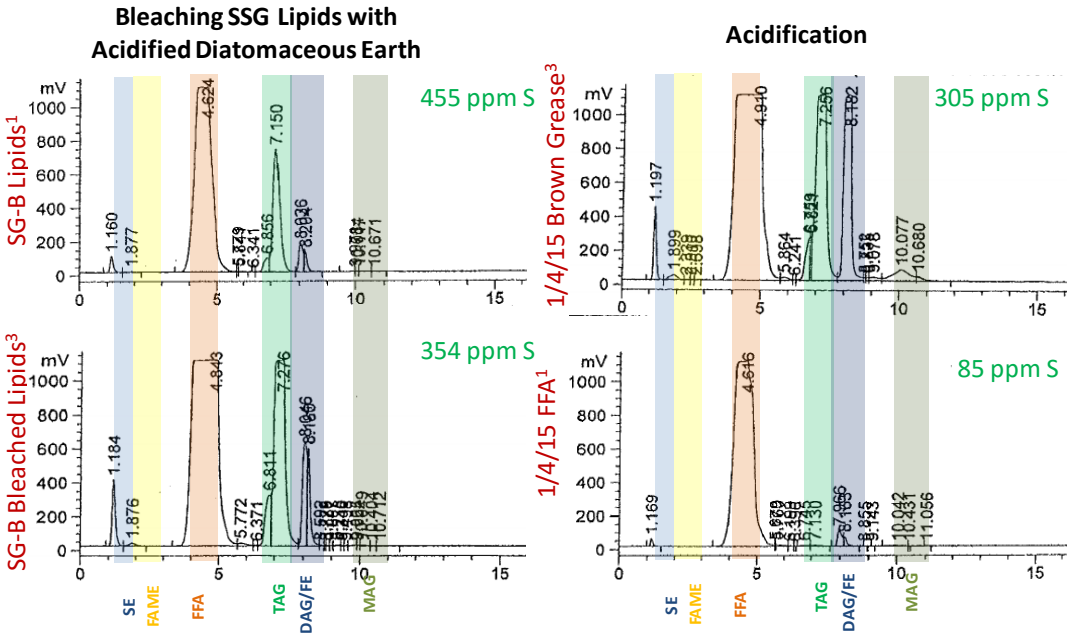
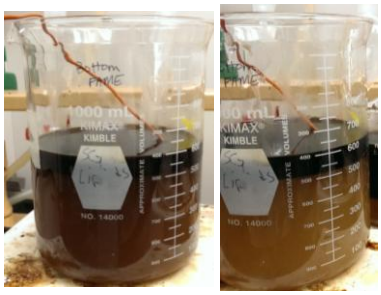


Figure B.2: Bleaching and acidification of brown grease lipids with corresponding sulfur contents.

The bleaching of SSG lipids showed a 22% reduction in sulfur content. The HPLC showed higher TAG/DAG peaks in the bleached lipids; however, this could be from the sensitivity of the machine from the overloaded samples and not an actual change in material composition. The acidification showed a 72% reduction in sulfur content and the peak at the acyl glycerides has almost disappeared because of the pretreatment process.

B.2. Emulsion Breaking

The emulsion produced in a sample of SSG crude FAME washing was experimented with to try to break the emulsion. Typically the emulsion will settle overnight but this is not efficient to do after each wash and to remove the entire emulsion layer and treat as waste results in lower yields. The interface between the emulsion and the water could be difficult to discern; therefore, the bottom portion and the emulsion layer of the first wash were heated and acidified. Water and FAME fractions were recorded. The pH, TAN, and soap number of the FAME were also analyzed. Figure B.3 shows the results of emulsion breaking. In Figure B.3, the left picture of each group represents the “before” treatment picture and the right picture represents the “after.” The bottom layer contained mostly water but contained 17% FAME and the emulsion layer contained 63% FAME resulting in a potential of 28% FAME recovery from the first wash. The biodiesel is high in TAN which is most likely due to the acid added to break the emulsion.



Wash 1 Bottom
Added 6.6 g acetic acid
4 mL 10% sulfuric acid
6 mL pure sulfuric acid
pH 2/3
Water ~ 500 mL
FAME ~ 100 mL
TAN: 74 mgKOH/gsample
Soap: 0 ppm

Wash 1 Emulsion
Added 1 mL pure sulfuric acid
pH 2/3
Water ~ 75 mL
FAME ~ 125 mL
TAN: 24 mgKOH/gsample
Soap: 0 ppm

Figure B.3: Emulsion Breaking Results.

Additional research should be performed to determine the necessary processing to reincorporate this recovered FAME into the production process. More water washes could reduce the TAN; basic washes would be more efficient, however this would most likely result in re-emulsifying the FAME. This material could be high in FFA which could benefit from a second esterification which could be recycled back to the bubble column reactor for further conversion.

B.3. Wiped-Film Evaporator (WFE) Cleaning Effect on Sulfur Content

In the wiped-film evaporation, the second pass distillate is the final product FAME. To be considered as biodiesel, this material must pass ASTM D6751 specifications; the sulfur specification is the most difficult to meet for biodiesel produced from brown grease. An experiment was performed to make sure that the second pass through the WFE would not affect the final sulfur content of the distillate. A sample of first pass residue was split in half and the first half was sent through the WFE without cleaning and the second half sent through the WFE after the WFE was cleaned with

hexane. The schematic of the GTW-to-biodiesel process used in this experiment is shown in Figure B.4.

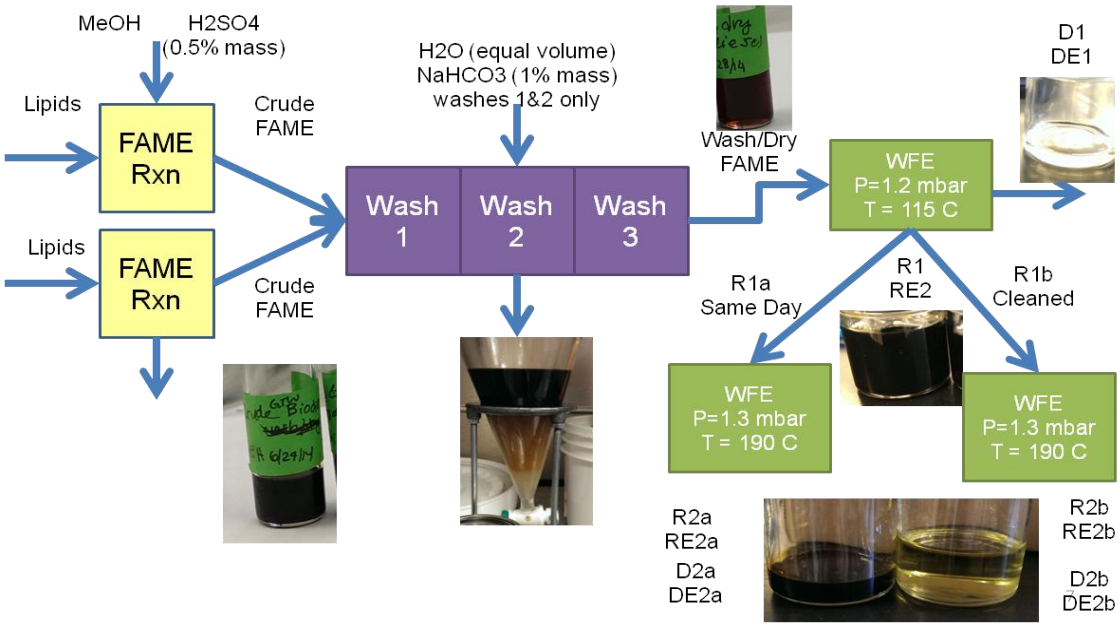


Figure B.4: GTW-to-biodiesel production process to analyze WFE cleaning effect on sulfur content.

Two batches of GTW were esterified in the bubble column reactor with methanol and 0.5% mass sulfuric acid. The crude biodiesel was washed twice with equal volume of water and 1% mass sodium bicarbonate (to neutralize the sulfuric acid). A third wash was done with only water. The washed biodiesel was dried overnight. Wash/Dry biodiesel was purified using a two-pass method in the wiped-film evaporator (WFE). The first pass was run at 1.2 mbar and 115 °C (300 °C AET) and a second pass was run at 1.3 mbar and 190 °C (400 °C AET). Residue (R) represents the high boiling point temperature liquid that stays on the hot-side while distillate (D) represents the low boiling point temperature liquid that vaporizes and is condensed. A transient flask (RE/DE) was

used to collect samples until flow/pressure was steady between operation changes. The first pass residue (R1) was split in half to determine if running two passes without cleaning in between would affect the sulfur content. Samples Pass 2a was run on the same day as Pass 1 with no cleaning of the WFE and Pass 2b was run after cleaning the column with hexane. Residue 2(a/b) is a viscous, dark brown material, while the distillate 2 (a/b) is a light yellow liquid and the final biodiesel product.

The sulfur content was measured using ThermoScientific TS 300 Total Sulfur Analyzer and TS-UV Module total sulfur detector on a 0-200 ppm S setting using method TSUV_E_Manual_Liquids1075. Calibrations were performed using triplicate testing of standard biodiesel samples from AccuStandard spiked with 15, 30, 75, and 200 ppm S. The sulfur content (ppm S) is shown in Figure B.5.

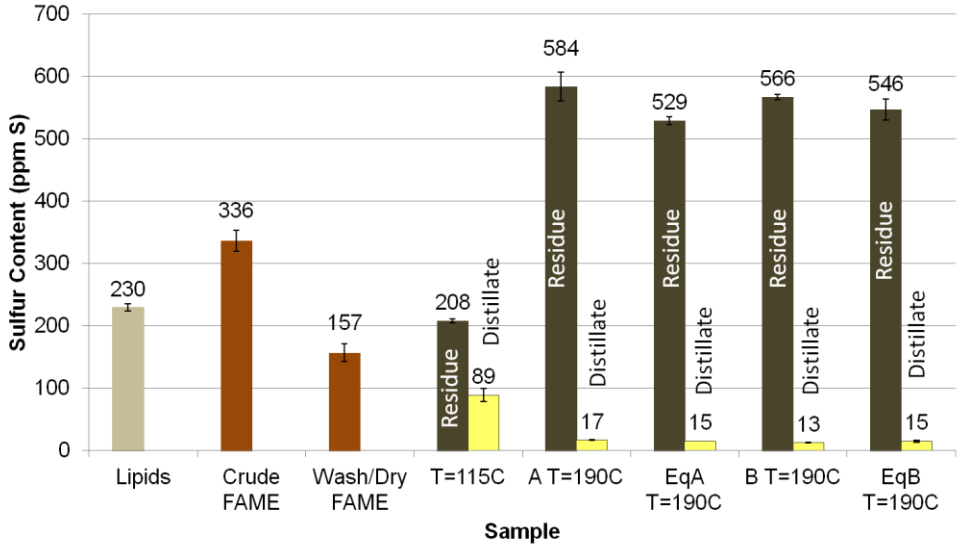


Figure B.5: Sulfur content of GTW-to-biodiesel process. T=115 ºC represents the first pass. T=190 ºC represents the second pass. A represents no cleaning of the WFE between passes and B represents cleaning of WFE between passes. Eq represents the transient flask until steady pressure/feed flow was reached in WFE.

Distillate A had higher sulfur content than Distillate B indicating that cleaning the column in between passes may reduce contamination of sulfur; however, the sulfur contents of the residues and the transient flasks do not show this trend. This result can further be analyzed using sulfur balances as shown in Figure B.6. The GTW lipids sulfur content compared to that of crude FAME did not significantly increase considering that 413 mg of sulfur was added with the sulfuric acid. It appears that sulfur content of crude biodiesel was not affected by the sulfuric acid catalyst. The sulfur content of the residue and distillate was the same regardless if the WFE was not cleaned (A) and the WFE was cleaned (B) in between Pass 1 and Pass 2.

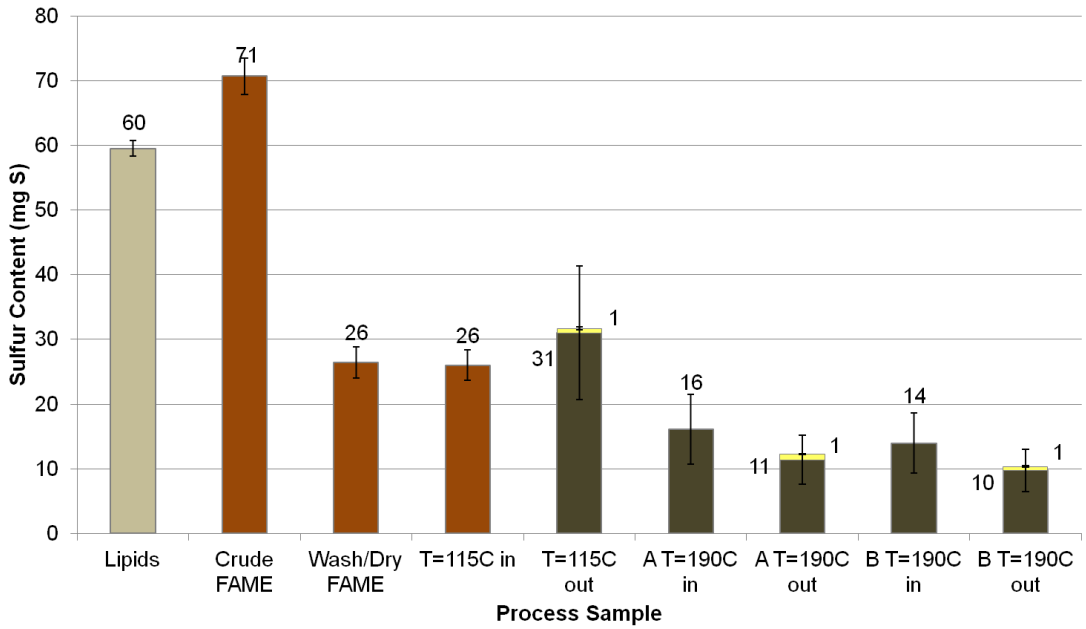


Figure B.6: Sulfur balance of GTW-to-biodiesel process. T=115 C represents the first pass. T=190 C represents the second pass. A represents no cleaning of the WFE between passes and B represents cleaning of WFE between passes.

B.4. Effect of One-Step v. Two-Step Reaction on Distillation Yield

Brown grease is composed of a high amount of free fatty acids (FFA) and low amount of acyl glycerides which require different reactions to convert into fatty acid methyl esters (FAME). Esterification reacts the FFA to FAME. Depending on the FFA content, to have a better yield of FAME, a second reaction could be needed to convert the remaining acyl glycerides into FAME using transesterification. An experiment was performed on a sample of brown grease to determine the effect that that a two-step reaction (esterification then transesterification) has on the purification process compared to a one-step reaction (esterification only). The process flow diagram is shown in Figure B.7.

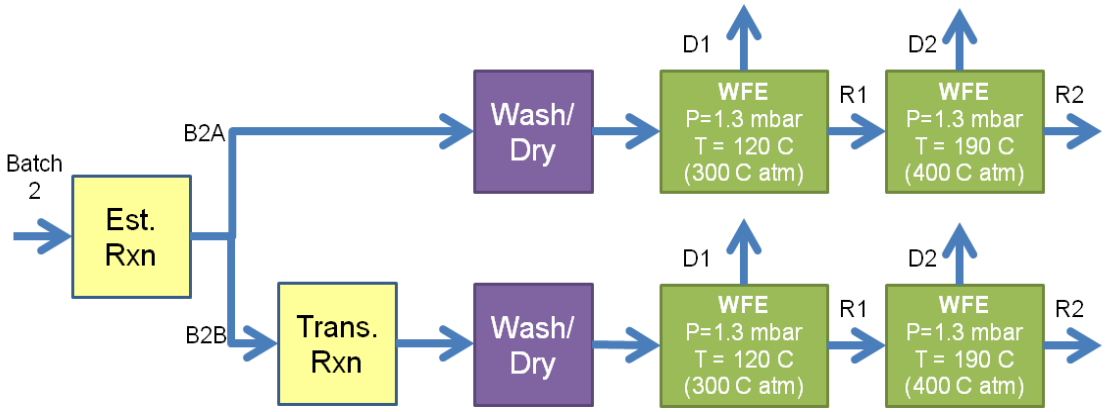


Figure B.7: Biodiesel process flow diagram for one-step versus two-step GTW-to-biodiesel process.

In the experiment, the crude biodiesel after the esterification was split in half (B2A and B2B). The first half (B2A) was washed and then purified using the standard two-pass WFE method. The second half (B2B) was transesterified, washed, and then purified using the two-pass WFE method. The yield and sulfur contents were taken

throughout the grease-to-biodiesel process. The yield of the distillation is shown in Figure B.8. The yields below represent the %mass of each fraction at each process stage and not from the beginning of distillation. For example, the Pass 2 yields are %mass of the mass of residue or distillate after Pass 2 divided by the amount put into the WFE for Pass 2.

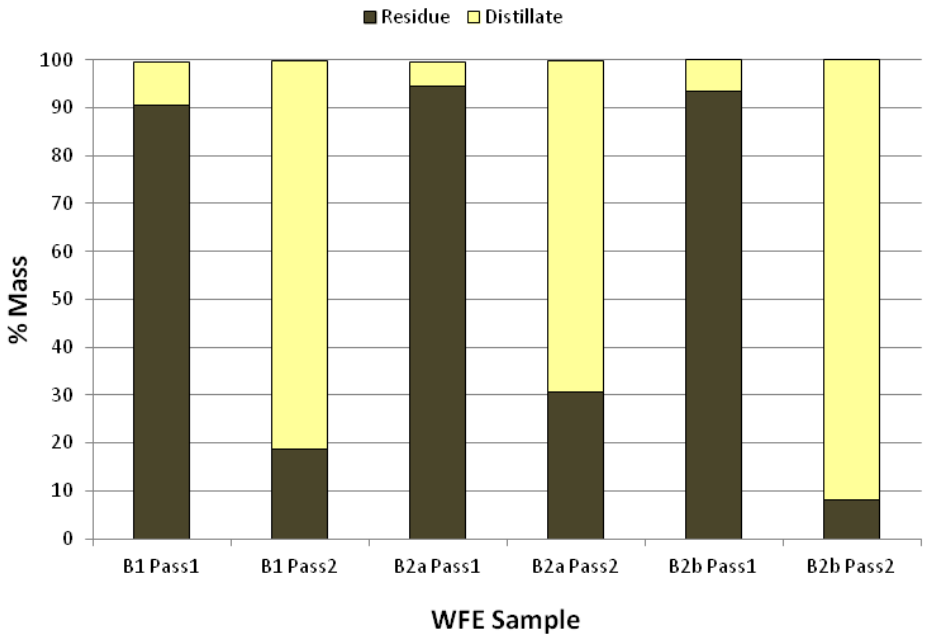


Figure B.8: Mass balance of purification processes for batch 1 and batch 2 FAME. Pass 1 represents 300 °C AET distillation and Pass 2 represents 400 °C AET distillation.

The first two columns (B1 Pass1 and B1 Pass2) were from a separate FAME purification on the same day as the two-step experiment. Comparing one-step (B2a) and two-step (B2b) Pass 1 columns showed similar yields (~95% residue) at the low-temperature distillation. The second high temperature distillation showed the benefits of the two-step reaction when it comes to yield. The one-step reaction distillate yield (B2a Pass2) had 70% distillate and 30% residue while the two-step distillate had 92% distillate and 8% residue. Tri-acylglycerides (TAG) have a high boiling point so it remains with

the residue in the one-step esterification reaction. When the TAG is converted to FAME, there is more distillate because there is less high-boiling point material in the crude FAME.

The sulfur of the second pass distillates was also determined for the one-step reaction and two-step reaction samples. The one-step reaction (B2a Pass 2) had a sulfur content of 18 ppm S while the two-step reaction (B2b Pass 2) had a sulfur content of 15 ppm S. These two samples are fairly similar in sulfur content and no conclusion can be made on the difference between the two trials due to the variability of the sulfur analyzer.

B.5. Distillation Results

The distillation results used in the comparative analysis is shown in Table B.1.

Table B.1: Distillation results.

Grease Type	Rxn Date	Purify Date	Method	Vacuum mBar	Temp. °C	AET °C	Yield D2 2nd pass (WFE)	Yield D2 start of distill	Lipid ppm S	Wash FAME ppm S	D1 ppm S	D2 ppm S	R2 ppm S	Sulfur Reduce (w/d)	Sulfur Reduce (lipid)	D2 TAN mgKOH/g
GTW	4/14/13; 5/31/13	7/8/2013	WFE	0.13	120	357	70%	70%	427	N/A	N/A	40	2608	N/A	91%	N/A
GTW	4/14/13; 5/31/13	7/8/2013	WFE	0.12	135	380	77%	77%	427	N/A	N/A	97	3997	N/A	77%	N/A
GTW	4/14/13; 5/31/13	7/8/2013	WFE	0.12	145	396	81%	81%	427	N/A	N/A	107	5371	N/A	75%	N/A
GTW	8/18/13; 8/20/13	8/22/2013	WFE	1.3	190	401	84%	79%	246	180	56	27	751	85%	89%	2.87
GTW	6/20/2014	6/30/2014	WFE	1.3	190	401	52%	49%	230	157	89	15	556	90%	93%	N/A
GTW	7/30/2014	8/4/2014	WFE	1.3	190	401	93%	82%	96	65	22	10	393	85%	90%	N/A
SSG	7/31/2014	8/4/2014	WFE	1.3	190	401	78%	57%	429	259	49	87	439	66%	80%	N/A
GTW	9/7/2014	9/15/2014	WFE	1.3	190	401	81%	73%	N/A	N/A	N/A	27.2	N/A	N/A	N/A	N/A
GTW	9/9/2014	9/15/2014	WFE	1.3	190	401	69%	65%	N/A	N/A	N/A	17.6	N/A	N/A	N/A	0.77
GTW	9/9/2014	9/15/2014	WFE	1.3	190	401	92%	86%	N/A	N/A	N/A	15	N/A	N/A	N/A	N/A
GTW	10/3/2014	10/17/2014	VacEvap	4	200	387	N/A	76%	N/A	118	N/A	15.1	434	87%	N/A	0.39
GTW	10/5/2014	10/23/2014	Rotovap	5	195	374	N/A	76%	409	183	N/A	N/A	N/A	N/A	N/A	N/A
GTW	10/5/2014	10/23/2014	Rotovap	3	198	391	N/A	81%	409	183	N/A	18	N/A	90%	96%	0.51
GTW	10/18/2014	10/24/2014	Rotovap	1	194	415	N/A	83%	303	N/A	N/A	19.9	N/A	N/A	93%	N/A
GTW	10/18/2014	10/26/2014	Rotovap	2	200	405	N/A	75%	303	80	N/A	12.3	416	85%	96%	N/A
GTW	10/18/2014	10/27/2014	WFE	1.3	190	401	82%	78%	303	80	N/A	26	1189	68%	91%	0.28
GTW	10/5/2014	10/27/2014	WFE	1.3	160	361	55%	51%	409	183	N/A	5.8	224	97%	99%	0.31
GTW	10/5/2014	10/27/2014	WFE	1.3	190	401	94%	89%	409	183	N/A	14.3	751	92%	97%	0.55
SSG	1/22/2015	1/27/2015	Rotovap	1.3	200	415	N/A	33%	474	143	32	76	474	47%	84%	N/A
GTW	12/21/2014	1/4/2015	Rotovap	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	24.1	N/A	N/A	N/A	N/A
GTW	12/21/2014	1/4/2015	Rotovap	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	26	N/A	N/A	N/A	N/A
SSG	1/29/2015	7/17/2014	Vigreaux	0.61	142	356	N/A	59%	455	364	504	36	1575	90%	92%	0.3
GTW	N/A	N/A	Vigreaux	N/A	128	346	N/A	64%	N/A	282	237	23	987	92%	N/A	0.49
GTW	6/29/2015	7/7/2015	Kugelrohr	0.93	180	398	N/A	79%	153	179	N/A	19	183	89%	88%	N/A
GTW	6/29/2015	7/9/2015	Kugelrohr	0.93	190	414	N/A	69%	153	179	N/A	16	235	91%	90%	N/A
GTW	6/29/2015	7/11/2015	Kugelrohr	0.93	200	426	77%	77%	153	179	N/A	21	445	88%	86%	N/A
GTW	6/29/2105	7/11/2015	Kugelrohr	0.93	200	426	34%	34%	153	226	N/A	26	265	88%	83%	N/A

B.6. Comparison of Means Using One-Way ANOVA

B.6.1. Grease Trap Waste versus Sewage Scum Grease

No significant difference was found between the means of each parameter and the type of brown grease (GTW and SSG). More samples of SSG are needed to verify these results.

Table B.2: Comparison of means for GTW and SSG.

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Vacuum (mBar)	Between Groups	.319	1	.319	.245	.625
	Within Groups	29.931	23	1.301		
	Total	30.250	24			
Vacuum (mmHg)	Between Groups	.180	1	.180	.245	.625
	Within Groups	16.836	23	.732		
	Total	17.016	24			
Max Temp. of Distillate (C)	Between Groups	22.110	1	22.110	.034	.856
	Within Groups	15120.530	23	657.414		
	Total	15142.640	24			
Max Temp of Distillate AET C	Between Groups	43.530	1	43.530	.093	.763
	Within Groups	10727.030	23	466.393		
	Total	10770.560	24			
Yield of Distillate	Between Groups	865.904	1	865.904	3.876	.061
	Within Groups	5138.505	23	223.413		
	Total	6004.410	24			
Yield of Residue	Between Groups	237.318	1	237.318	1.364	.256
	Within Groups	3655.000	21	174.048		
	Total	3892.318	22			
Distillate PPM Sulfur	Between Groups	4094.139	1	4094.139	6.584	.017
	Within Groups	14923.332	24	621.806		
	Total	19017.471	25			
Cold Trap	Between Groups	3018424.500	1	3018424.500	.	.
	Within Groups	.000	0	.		
	Total	3018424.500	1			
Sulfur Reduction (from w/d)	Between Groups	1073.041	1	1073.041	10.319	.005
	Within Groups	1663.842	16	103.990		
	Total	2736.883	17			
Sulfur reduction (from lipid)	Between Groups	61.426	1	61.426	1.307	.268
	Within Groups	845.836	18	46.991		
	Total	907.262	19			
TAN Distillate	Between Groups	.197	1	.197	.266	.622
	Within Groups	5.200	7	.743		
	Total	5.398	8			

B.6.2. Distillation Equipment

No significant difference was found between the means of each parameter and the type of distillation equipment.

Table B.3: Comparison of means for distillation equipment.

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Yield of Distillate	Between Groups	847.366	4	211.842	.822	.527
	Within Groups	5157.043	20	257.852		
	Total	6004.410	24			
Yield of Residue	Between Groups	977.466	3	325.822	2.124	.131
	Within Groups	2914.852	19	153.413		
	Total	3892.318	22			
Distillate PPM Sulfur	Between Groups	1272.655	4	318.164	.377	.823
	Within Groups	17744.816	21	844.991		
	Total	19017.471	25			
Sulfur Reduction (from w/d)	Between Groups	255.168	4	63.792	.334	.850
	Within Groups	2481.714	13	190.901		
	Total	2736.883	17			
Sulfur reduction (from lipid)	Between Groups	151.260	3	50.420	1.067	.391
	Within Groups	756.002	16	47.250		
	Total	907.262	19			
TAN Distillate	Between Groups	.643	3	.214	.225	.875
	Within Groups	4.755	5	.951		
	Total	5.398	8			

Appendix C. Well-to-Wheel Life Cycle of Biodiesel Produced from Grease Trap Waste

C.1. 100-year Global Warming Potential Consequential Life Cycle Assessment

The table below lists the data for the GWP_{100} used for the consequential analysis in Figure 4.5 of Section 4.3.1.2.

Table C.1: GWP_{100} consequential LCA for flare scenario.

Lipid Content	2%	3%	4%	5%	7%	10%	20%	30%	40%
Proposed GTW-Biodiesel Process									
Delivery to Transfer Station	44	29	22	18	13	9	4	3	2
Pretreatment WM	131	87	65	52	37	25	12	8	6
GTW-Biodiesel Rest of Process	50	40	35	31	28	25	22	21	20
Total GTW-Biodiesel Process	***226***	***156***	***122***	***101***	***77***	***59***	***39***	***32***	***28***
Current GTW Process									
Delivery to Transfer Station	44	29	22	18	13	9	4	3	2
Current GTW Disposal	139	95	73	60	45	33	20	16	13
Low Sulfur Diesel	93	93	93	93	93	93	93	93	93
Total Displaced Current GTW Process	***276***	***217***	***188***	***170***	***150***	***135***	***117***	***111***	***108***
Total GTW-Biodiesel - Total Current GTW Disposal	**-50**	**-61**	**-66**	**-69**	**-73**	**-75**	**-78**	**-80**	**-80**

Table C.2: GWP_{100} consequential LCA for cogeneration scenario.

Lipid Content	2%	3%	4%	5%	7%	10%	20%	30%	40%
Proposed GTW-Biodiesel Process									
Delivery to Transfer Station	44	29	22	18	13	9	4	3	2
Pretreatment WM	175	116	87	69	49	34	17	11	8
Biodiesel Co-Gen Avoided Utilities	-107	-71	-54	-43	-31	-21	-11	-7	-5
GTW-Biodiesel Rest of Process	50	40	35	31	28	25	22	21	20
Total GTW-Biodiesel Process	***162***	***114***	***90***	***76***	***59***	***47***	***32***	***27***	***25***
Current GTW Process									
Delivery to Transfer Station	44	29	22	18	13	9	4	3	2
Current GTW Disposal	185	126	97	79	59	44	26	21	18
Current GTW Co-Gen Avoided Utilities	-112	-77	-59	-48	-36	-27	-16	-13	-11
Low Sulfur Diesel	93	93	93	93	93	93	93	93	93
Total Displaced Current GTW Process	***209***	***171***	***153***	***141***	***128***	***119***	***107***	***104***	***102***
Total GTW-Biodiesel - Total Current GTW Disposal	**-47**	**-57**	**-63**	**-66**	**-69**	**-72**	**-75**	**-76**	**-77**

C.2. Attributional LCA

Presented below are the results for all environmental impacts for GTW-biodiesel for scenarios with landfill gas flaring, landfill gas cogeneration of heat and electricity, and a scenario without GTW waste management (omits impacts associated with delivery of GTW to the transfer station and GTW wastewater and waste solids disposal. These results are compared to soybean-biodiesel and LSD. Note that the values of soybean-biodiesel and LSD do not change with each GTW scenario.

C.2.1. Soybean Biodiesel and Low-sulfur Diesel (LSD)

The two tables below represent are the results of GREET2014 for soybean-biodiesel and LSD.

Table C.3: Soybean biodiesel data.

	GWP_{100}	CED_{Fossil}	Carbon Monoxide	Particulate Matter	Mono-nitrogen Oxides	Sulfur Oxides
Unit	g-CO_2-eq/MJ-fuel	MJ/MJ-fuel	g-CO/MJ-fuel	g-PM/MJ-fuel	g-NOx/MJ-fuel	g-SOx/MJ-fuel
Soybean Production	5.663	0.049	0.010	0.002	0.018	0.017
Soy Oil Extraction	4.241	0.056	0.003	0.001	0.006	0.010
Soy oil Transportation	0.721	0.009	0.002	0.000	0.007	0.001
Pretreatment Total	**10.625**	**0.113**	**0.014**	**0.003**	**0.032**	**0.028**
Soy oil Conversion	9.117	0.138	0.004	0.001	0.008	0.008
Biodiesel Transportation	0.510	0.006	0.001	0.000	0.004	0.001
Biodiesel Storage	0.000	0.000	0.000	0.000	0.000	0.000
Fuel Production Total	**9.627**	**0.144**	**0.004**	**0.002**	**0.011**	**0.009**
Vehicle Operation	4.794	0.000	0.066	0.001	0.037	0.000
Total	**25.046**	**0.257**	**0.085**	**0.006**	**0.080**	**0.037**

Table C.4: Low-sulfur diesel data.

	GWP_{100}	CED_{Fossil}	Carbon Monoxide	Particulate Matter	Mono-nitrogen Oxides	Sulfur Oxides
	g-CO_2-eq/MJ-fuel	MJ/MJ-fuel	g-CO/MJ-fuel	g-PM/MJ-fuel	g-NOx/MJ-fuel	g-SOx/MJ-fuel
Heavy Butane from Crude Oil	0.001	0.000	0.000	0.000	0.000	0.000
Crude Recovery for U.S. Refineries	8.744	0.079	0.008	0.002	0.025	0.013
Well/Pretreatment Total	**8.744**	**0.079**	**0.008**	**0.002**	**0.025**	**0.013**
LSD Refining	7.890	0.123	0.005	0.002	0.010	0.008
Processing LSD	0.463	0.005	0.001	0.000	0.003	0.001
LSD Storage	0.000	0.000	0.000	0.000	0.000	0.000
Fuel Production/ Processing Total	**8.353**	**0.128**	**0.005**	**0.002**	**0.013**	**0.009**
Vehicle Operation	**75.717**	**1.000**	**0.128**	**0.002**	**0.033**	**0.001**
LSD Total	**92.814**	**1.207**	**0.141**	**0.006**	**0.071**	**0.022**

C.2.2. 100-year Global Warming Potential

Figure C.1. shows GWP_{100} for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process.

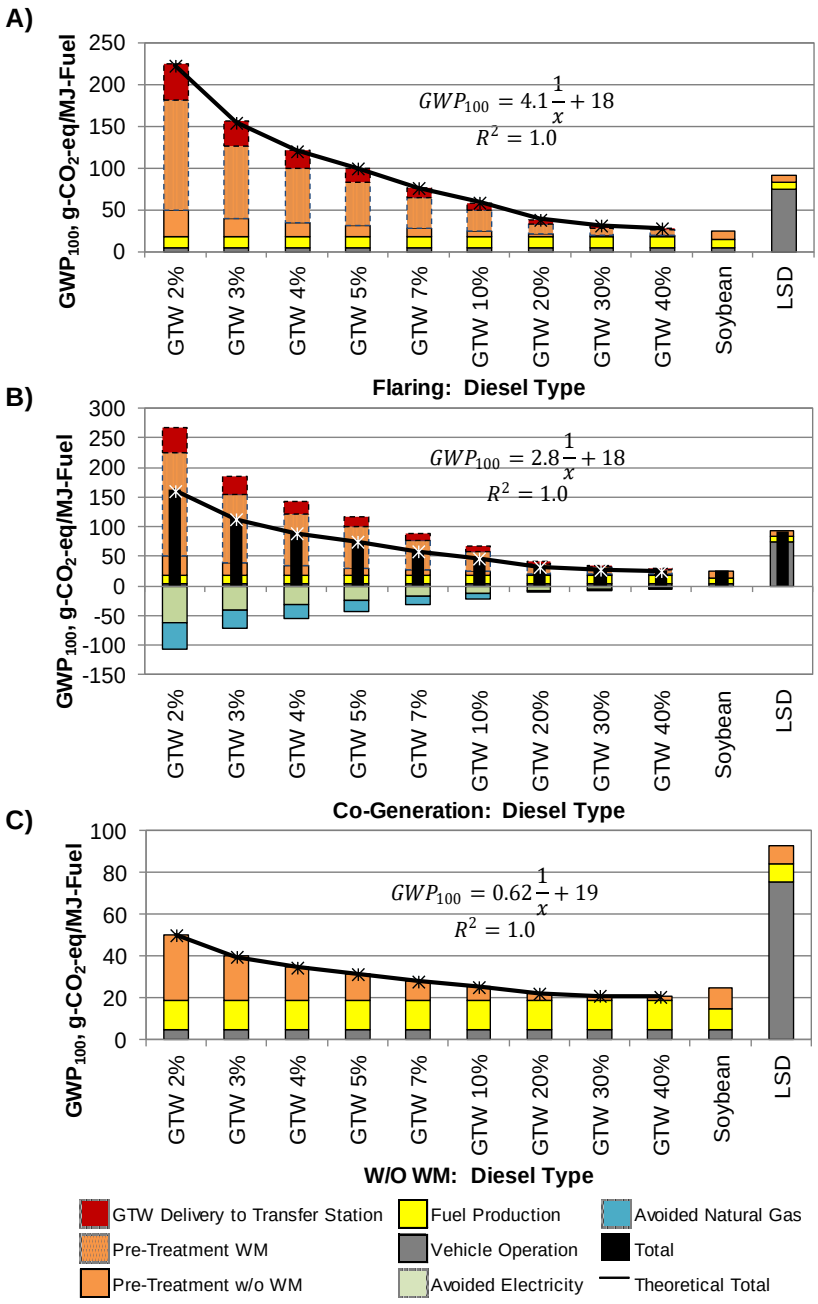


Figure C.1: 100-y global warming potential complete parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD for A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total GWP_{100} (black bar) and modeled curve (black line) are also shown.

The following tables show the GWP_{100} value by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.5: Landfill gas flaring scenario for 100-y global warming potential.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
GWP_{100}, g-CO_2-eq/MJ-fuel											
Delivery to Transfer Station	44	29	22	18	13	8	4	3	2	N/A	N/A
Pretreatment WM	131	87	65	52	37	25	12	8	6	N/A	N/A
Pretreatment w/o WM	31	21	16	13	9	6	3	2	1	11	9
Fuel Production	14	14	14	14	14	14	14	14	14	10	8
Vehicle Operation	5	5	5	5	5	5	5	5	5	5	5
Total	226	156	122	101	77	59	39	32	28	25	93
Percent Contribution, %											
Delivery to Transfer Station	20	19	18	17	16	15	11	9	7	N/A	N/A
Pretreatment WM	58	56	54	51	48	43	32	25	20	N/A	N/A
Pretreatment w/o WM	14	13	13	12	12	10	8	6	5	42	9
Fuel Production	6	9	12	14	18	24	37	45	50	38	9
Vehicle Operation	2	3	4	5	6	8	12	15	17	19	82
Reduction, %											
Compared to Soybean	802	525	386	303	208	137	54	26	13	0	271
Compared to LSD	143	69	31	9	-17	-36	-58	-66	-70	-73	0

Table C.6: Landfill gas with cogeneration scenario for 100-y global warming potential.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
GWP_{100}, g-CO_2-eq/MJ-fuel											
Delivery to Transfer Station	44	29	22	18	13	9	4	3	2	N/A	N/A
Pretreatment WM	175	116	87	69	49	34	17	11	8	N/A	N/A
Pretreatment w/o WM	31	21	16	13	9	6	3	2	1	11	9
Fuel Production	14	14	14	14	14	14	14	14	14	10	8
Vehicle Operation	5	5	5	5	5	5	5	5	5	5	78
Avoided Electricity	-62	-41	-31	-25	-18	-12	-6	-4	-3	N/A	N/A
Avoided Natural Gas	-45	-30	-23	-18	-13	-9	-5	-3	-2	N/A	N/A
Total	162	114	90	76	59	57	32	27	25	25	93
Percent Contribution, %											
Delivery to Transfer Station	27	26	24	23	21	19	13	10	8	N/A	N/A
Pretreatment w/o WM	19	18	17	17	15	13	9	7	6	42	9
Fuel Production	9	12	16	19	24	30	44	52	57	38	9
Vehicle Operation	3	4	5	6	8	10	15	17	19	19	82
Avoided Electricity	-38	-36	-34	-33	-30	-26	-19	-15	-12	N/A	N/A
Avoided Natural Gas	-28	-27	-25	-24	-22	-19	-14	-11	-9	N/A	N/A
Reduction, %											
Compared to Soybean	547	355	259	201	136	86	29	9	0	0	271
Compared to LSD	75	23	-3	-19	-36	-50	-65	-70	-73	-73	0

Table C.7: Without GTW waste management scenario for 100-y global warming potential.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
GWP_{100}, $g\text{-}CO_2\text{-}eq/MJ\text{-}fuel											
Pretreatment	31	21	16	13	9	6	3	2	2	11	9
Fuel Production	14	14	14	14	14	14	14	14	14	10	8
Vehicle Operation	5	5	5	5	5	5	5	5	5	5	76
Total	50	40	35	32	28	25	22	21	20	25	93
Percent Contribution, %											
Pretreatment	62	52	45	40	32	25	14	9	7	42	9
Fuel Production	28	36	41	45	51	56	64	68	69	38	9
Vehicle Operation	10	12	14	15	17	19	22	23	23	19	82
Reduction, %											
Compared to Soybean	101	59	38	26	11	1	-12	-16	-18	0	271
Compared to LSD	-46	-57	-63	-66	-70	-73	-76	-77	-78	-73	0

C.2.3. Fossil Cumulative Energy Demand (CED_{Fossil})

The fossil cumulative energy demand (fossil CED) was determined for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process shown in Figure C.2.

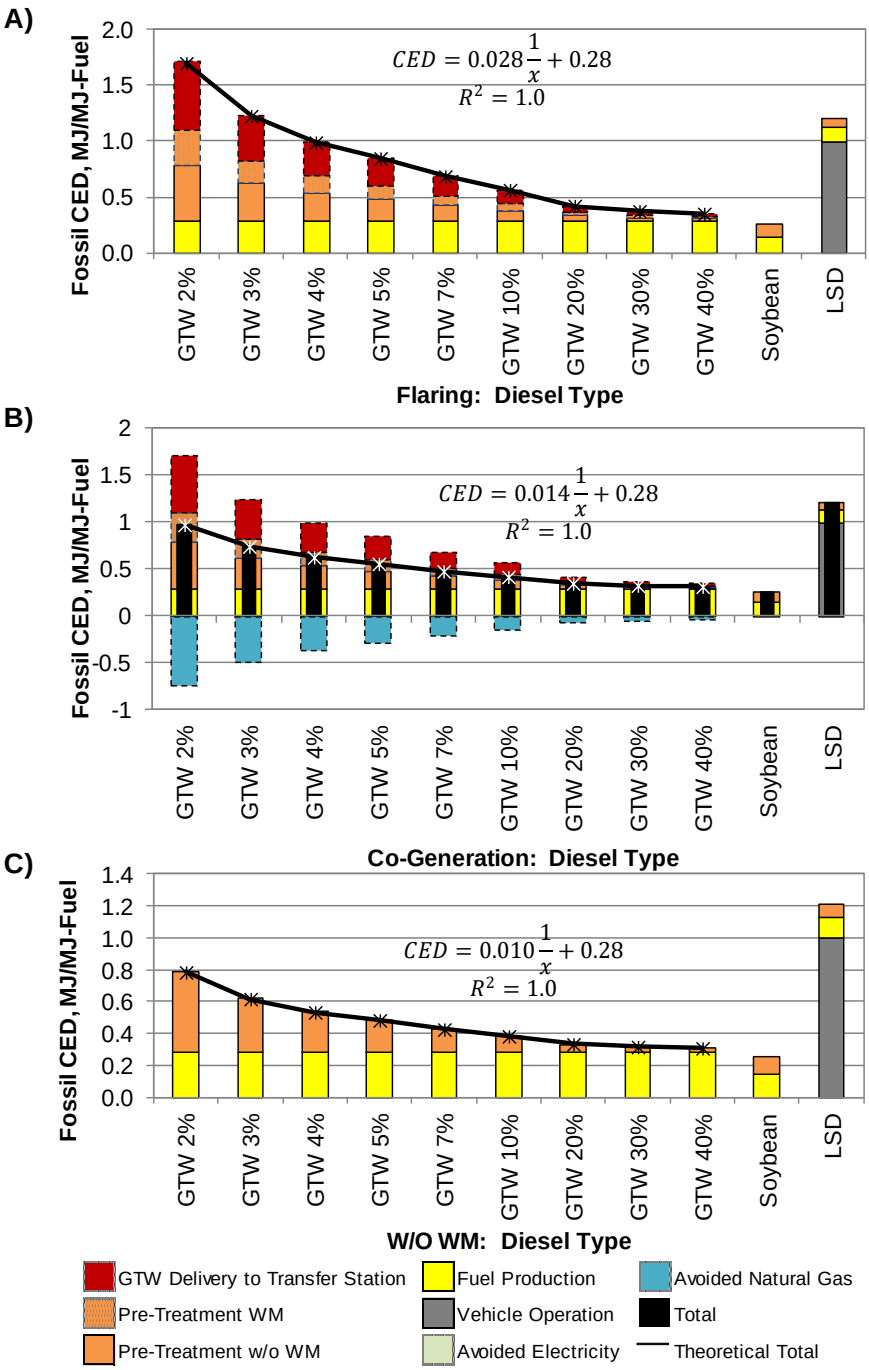


Figure C.2: Fossil cumulative energy demand complete parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD for A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total CED_{Fossil} (black bar) and modeled curve (black line) are also shown.

The following tables show the CED_{Fossil} value by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.8: Landfill gas with flaring scenario for fossil cumulative energy demand.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Fossil CED, MJ/MJ-Fuel											
Delivery to Transfer Station	0.62	0.41	0.31	0.25	0.18	0.12	0.06	0.04	0.03	N/A	N/A
Pretreatment WM	0.31	0.20	0.15	0.12	0.08	0.06	0.03	0.02	0.01	N/A	N/A
Pretreatment w/o WM	0.51	0.34	0.25	0.20	0.14	0.10	0.05	0.03	0.02	0.11	0.08
Fuel Production	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.14	0.13
Vehicle Operation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
Total	1.72	1.24	1.00	0.85	0.69	0.56	0.42	0.37	0.35	0.26	1.21
Percent Contribution, %											
Delivery to Transfer Station	36	33	31	29	26	22	14	11	9	N/A	N/A
Pretreatment WM	18	16	15	14	12	10	6	4	3	N/A	N/A
Pretreatment w/o WM	29	27	25	24	21	18	12	8	7	44	7
Fuel Production	17	23	29	33	41	50	68	76	82	56	11
Vehicle Operation	0	0	0	0	0	0	0	0	0	0	83
Reduction, %											
Compared to Soybean	568	381	287	231	167	119	63	45	35	0	370
Compared to LSD	42	2	-18	-29	-43	-53	-65	-69	-71	-79	0

Table C.9: Landfill gas with cogeneration scenario for fossil cumulative energy demand.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Fossil CED, MJ/MJ-fuel											
Delivery to Transfer Station	0.62	0.41	0.31	0.25	0.18	0.12	0.06	0.04	0.03	N/A	N/A
Pretreatment WM	0.31	0.20	0.15	0.12	0.08	0.06	0.03	0.02	0.01	N/A	N/A
Pretreatment w/o WM	0.51	0.34	0.25	0.20	0.14	0.10	0.05	0.03	0.02	0.11	0.08
Fuel Production	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.14	0.13
Vehicle Operation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
Avoided Electricity	-0.01	-0.004	-0.003	-0.003	-0.002	-0.001	-0.001	<-0.001	<-0.001	N/A	N/A
Avoided Natural Gas	-0.73	-0.49	-0.37	-0.29	-0.21	-0.15	-0.07	-0.05	-0.04	N/A	N/A
Total	0.98	0.74	0.63	0.56	0.48	0.42	0.35	0.32	0.31	0.26	1.21
Percent Contribution, %											
Delivery to Transfer Station	63	55	49	44	37	30	18	12	10	N/A	N/A
Pretreatment WM	31	27	24	22	18	14	8	5	4	N/A	N/A
Pretreatment w/o WM	52	45	40	36	30	24	14	10	7	44	7
Fuel Production	29	38	45	51	60	68	82	88	91	56	11
Vehicle Operation	0	0	0	0	0	0	0	0	0	0	83
Avoided Electricity	-1	-1	-1	-1	<-1	<-1	<-1	<-1	<-1	N/A	N/A
Avoided Natural Gas	-75	65	58	53	-44	-35	-21	-15	-12	N/A	N/A
Reduction, %											
Compared to Soybean	281	190	144	117	85	62	35	25	21	0	370
Compared to LSD	-19	-38	-48	-54	-61	-66	-71	-73	-74	-79	0

Table C.10: Without GTW waste management scenario for fossil cumulative energy demand.

Lipid Content	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Fossil CED, MJ/MJ-fuel											
Pretreatment	0.51	0.34	0.25	0.20	0.14	0.10	0.05	0.03	0.02	0.11	0.08
Fuel Production	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.14	0.13
Vehicle Operation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
Total	0.79	0.62	0.54	0.48	0.43	0.38	0.33	0.32	0.31	0.26	1.21
Percent Contribution, %											
Pretreatment	64	54	47	41	33	26	15	10	7	44	7
Fuel Production	36	46	53	59	67	74	85	90	93	56	11
Vehicle Operation	0	0	0	0	0	0	0	0	0	0	83
Reduction, %											
Compared to Soybean	207	141	108	89	66	49	29	23	19	0	370
Compared to LSD	-35	-49	-56	-60	-65	-68	-72	-74	-75	-79	0

C.2.4. Carbon Monoxide

The carbon monoxide (CO) emissions were determined for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process shown in Figure C.3.

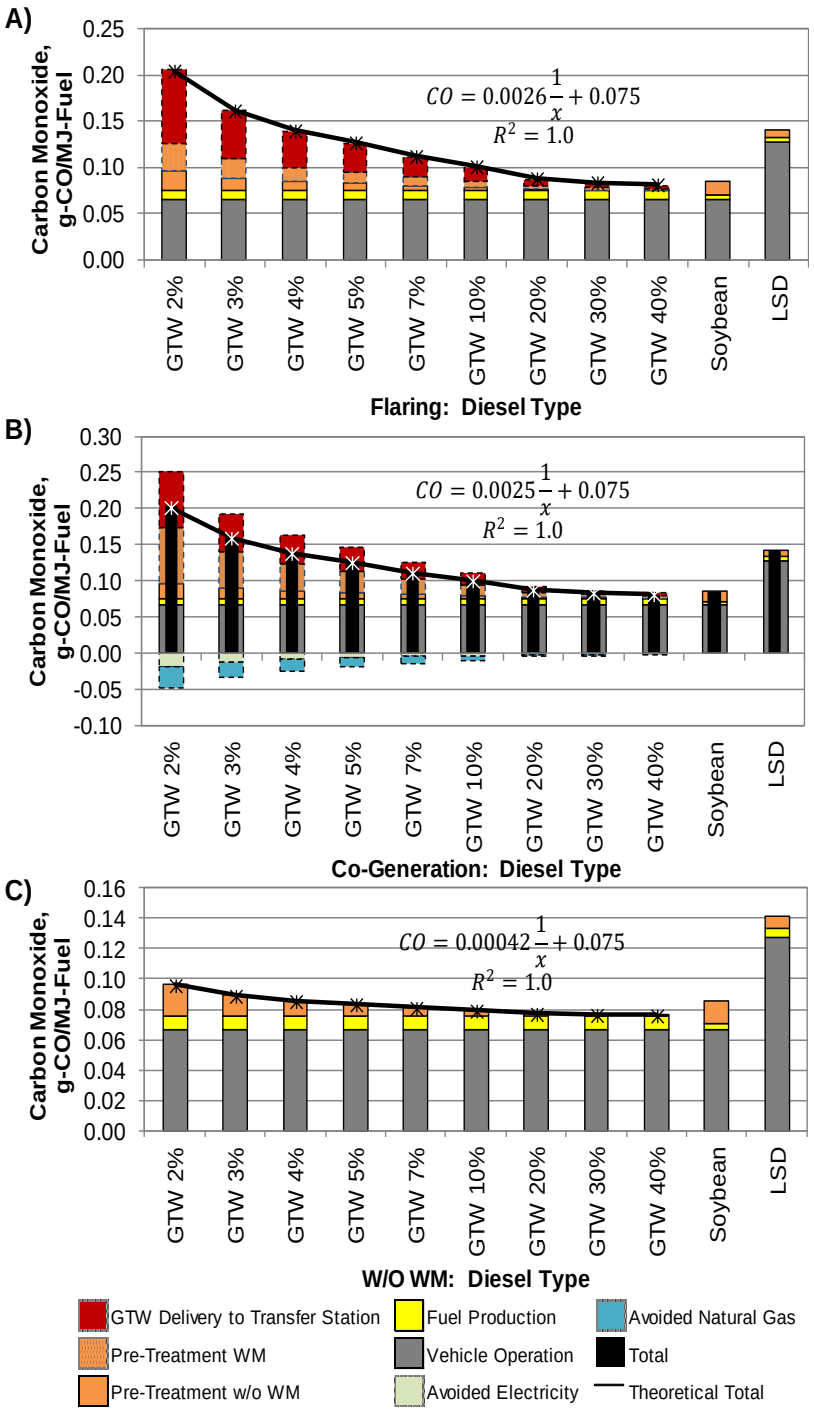


Figure C.3: Carbon monoxide complete emissions parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total CO (black bar) and modeled curve (black line) are also shown.

The following tables show the CO emissions by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.11 Landfill gas flaring scenario for carbon monoxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Carbon Monoxide, g-CO/MJ-Fuel											
Delivery to Transfer Station	0.079	0.053	0.039	0.032	0.022	0.016	0.008	0.005	0.004	N/A	N/A
Pretreatment WM	0.030	0.020	0.015	0.012	0.009	0.006	0.003	0.002	0.001	N/A	N/A
Pretreatment w/o WM	0.021	0.014	0.011	0.008	0.006	0.004	0.002	0.001	0.001	0.014	0.008
Fuel Production	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.004	0.005
Vehicle Operation	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.128
Total	0.206	0.162	0.140	0.127	0.112	0.101	0.088	0.083	0.081	0.085	0.141
Percent Contribution, %											
Delivery to Transfer Station	38	33	28	25	20	16	9	6	5	N/A	N/A
Pretreatment WM	10	9	8	7	5	4	2	2	1	N/A	N/A
Pretreatment w/o WM	15	12	11	9	8	6	3	2	1	17	6
Fuel Production	4	5	6	7	8	9	10	11	11	5	4
Vehicle Operation	32	41	47	52	59	66	76	80	82	78	90
Reduction, %											
Compared to Soybean	142	90	65	49	32	18	3	-2	-5	0	66
Compared to LSD	46	15	-1	-10	-21	-29	-38	-41	-43	-40	0

Table C.12: Landfill gas cogeneration scenario for carbon monoxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Carbon Monoxide, g-CO/MJ-fuel											
Delivery to Transfer Station	0.079	0.053	0.039	0.032	0.022	0.016	0.008	0.005	0.004	N/A	N/A
Pretreatment WM	0.076	0.051	0.038	0.030	0.022	0.015	0.007	0.005	0.004	N/A	N/A
Pretreatment w/o WM	0.021	0.014	0.011	0.008	0.006	0.004	0.002	0.001	0.001	0.014	0.008
Fuel Production	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.004	0.005
Vehicle Operation	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.128
Avoided Electricity	-0.018	-0.012	-0.009	-0.007	-0.005	-0.004	-0.002	-0.001	-0.001	N/A	N/A
Avoided Natural Gas	-0.031	-0.020	-0.015	-0.012	-0.009	-0.006	-0.003	-0.002	-0.002	N/A	N/A
Total	0.203	0.160	0.139	0.126	0.111	0.100	0.087	0.083	0.081	0.085	0.141
Percent Contribution, %											
Delivery to Transfer Station	39	33	28	25	20	16	9	6	5	N/A	N/A
Pretreatment WM	38	32	27	24	19	15	8	6	4	N/A	N/A
Pretreatment w/o WM	10	9	8	7	5	4	2	2	1	17	6
Fuel Production	4	5	6	7	8	9	10	11	11	5	4
Vehicle Operation	33	41	48	53	60	66	76	80	82	78	90
Avoided Electricity	-9	-8	-7	-6	-5	-4	-2	-1	-1	N/A	N/A
Avoided Natural Gas	-15	-13	-11	-10	-8	-6	-4	-2	-2	N/A	N/A
Reduction, %											
Compared to Soybean	139	88	63	48	31	18	3	-2	-5	0	66
Compared to LSD	44	13	-2	-11	-21	-29	-38	-41	-43	-40	0

Table C.13: Without GTW waste management scenario for carbon monoxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Carbon Monoxide, g-CO/MJ-fuel											
Pretreatment	0.021	0.014	0.011	0.008	0.006	0.004	0.002	0.001	0.001	0.014	0.008
Fuel Production	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.004	0.005
Vehicle Operation	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.066	0.128
Total	0.096	0.089	0.086	0.083	0.081	0.079	0.077	0.076	0.076	0.085	0.141
Percent Contribution, %											
Pretreatment	22	16	12	10	7	5	3	2	1	17	6
Fuel Production	9	10	10	10	11	11	11	11	12	5	4
Vehicle Operation	69	74	77	79	82	84	86	87	87	78	90
Reduction, %											
Compared to Soybean	13	5	1	-2	-5	-7	-9	-10	-11	0	66
Compared to LSD	-32	-37	-39	-41	-43	-44	-45	-46	-46	-40	0

C.2.5. Particulate Matter

The particulate matter (PM) emissions were determined for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process shown in Figure C.4.

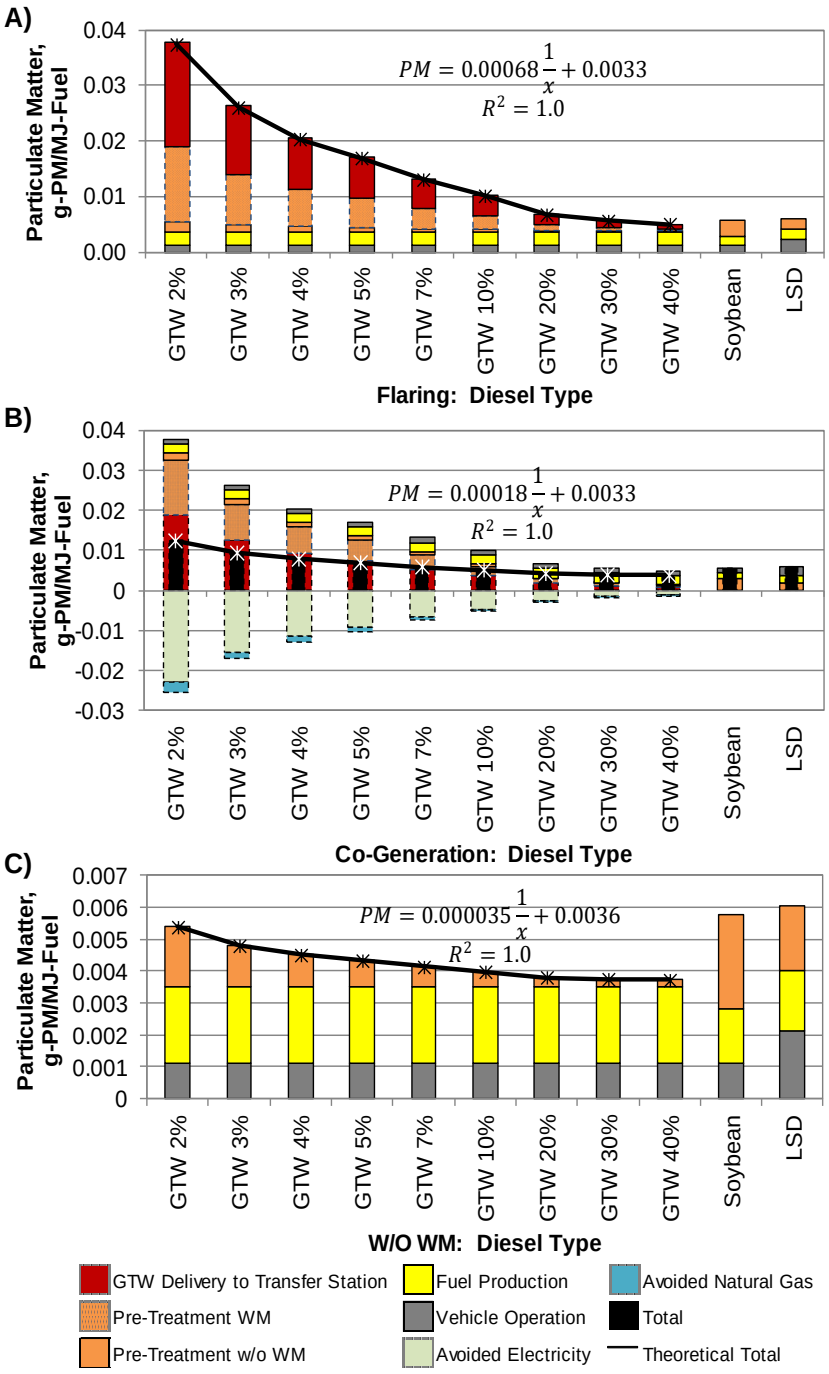


Figure C.4: Particulate matter complete parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD for A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total PM (black bar) and modeled curve (black line) are also shown.

The following tables show the PM emissions by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.14: Landfill gas flaring scenario for particulate matter emissions.

Diesel Types	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Particulate Matter, g-PM/MJ-Fuel											
Delivery to Transfer Station	0.019	0.012	0.009	0.007	0.005	0.004	0.002	0.001	0.001	N/A	N/A
Pretreatment WM	0.014	0.009	0.007	0.005	0.004	0.002	0.001	0.001	0.000	N/A	N/A
Pretreatment w/o WM	0.002	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.003	0.001
Fuel Production	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002
Total	0.038	0.026	0.021	0.017	0.013	0.010	0.007	0.006	0.005	0.006	0.006
Percent Contribution, %											
Delivery to Transfer Station	50	48	46	44	40	37	27	22	18	N/A	N/A
Pretreatment WM	36	34	32	31	28	24	16	11	7	N/A	N/A
Pretreatment w/o WM	5	5	5	5	5	5	4	4	4	52	33
Fuel Production	6	9	12	14	18	23	36	43	48	29	31
Vehicle Operation	3	4	5	7	9	11	17	20	23	19	35
Reduction, %											
Compared to Soybean	553	354	254	195	128	76	16	-4	-14	0	5
Compared to LSD	523	334	238	181	117	68	11	-8	-18	-5	0

Table C.15: Landfill gas cogeneration scenario for particulate matter emissions.

Lipid Content	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Carbon Monoxide, g-CO/MJ-fuel											
Delivery to Transfer Station	0.019	0.012	0.009	0.007	0.005	0.004	0.002	0.001	0.001	N/A	N/A
Pretreatment WM	0.014	0.009	0.007	0.005	0.004	0.002	0.001	0.001	0.000	N/A	N/A
Pretreatment w/o WM	0.002	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.003	0.002
Fuel Production	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002
Avoided Electricity	-0.023	-0.015	-0.011	-0.009	-0.006	-0.005	-0.002	-0.002	-0.001	N/A	N/A
Avoided Natural Gas	-0.003	-0.002	-0.001	-0.001	-0.001	-0.001	0.000	0.000	0.000	N/A	N/A
Total	0.012	0.009	0.008	0.007	0.006	0.005	0.004	0.004	0.004	0.006	0.006
Percent Contribution, %											
Delivery to Transfer Station	150	133	119	108	90	73	44	31	24	N/A	N/A
Pretreatment WM	109	96	85	76	63	48	25	15	10	N/A	N/A
Pretreatment w/o WM	15	14	13	12	11	9	7	6	5	52	33
Fuel Production	19	25	30	34	40	47	57	62	64	29	31
Vehicle Operation	9	12	14	16	19	22	27	29	30	19	35
Avoided Electricity	-182	-161	-145	-131	-109	-89	-54	-39	-31	N/A	N/A
Avoided Natural Gas	-21	-18	-16	-15	-12	-10	-6	-4	-3	N/A	N/A
Reduction, %											
Compared to Soybean	116	63	36	20	3	-12	-28	-33	-36	0	5
Compared to LSD	106	55	30	14	-2	-16	-31	-36	-39	-5	0

Table C.16: Without GTW waste management scenario for particulate matter emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Particulate Matter, g-PM/MJ-fuel											
Delivery to Transfer Station	0.019	0.012	0.009	0.007	0.005	0.004	0.002	0.001	0.001	N/A	N/A
Pretreatment	0.002	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.003	0.002
Fuel Production	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002
Total	0.005	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.006
Percent Contribution, %											
Pretreatment	35	27	22	19	15	12	8	6	5	52	33
Fuel Production	44	49	53	55	58	60	63	64	64	29	31
Vehicle Operation	21	23	25	26	27	28	30	30	30	19	35
Reduction, %											
Compared to Soybean	-7	-17	-22	-25	-29	-31	-34	-35	-36	0	5
Compared to LSD	-11	-21	-26	-28	-32	-34	-37	-38	-39	-5	0

C.2.6. Mono-Nitrogen Oxide

The mono-nitrogen oxide (NO_x) emissions were determined for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process shown in Figure C.5.

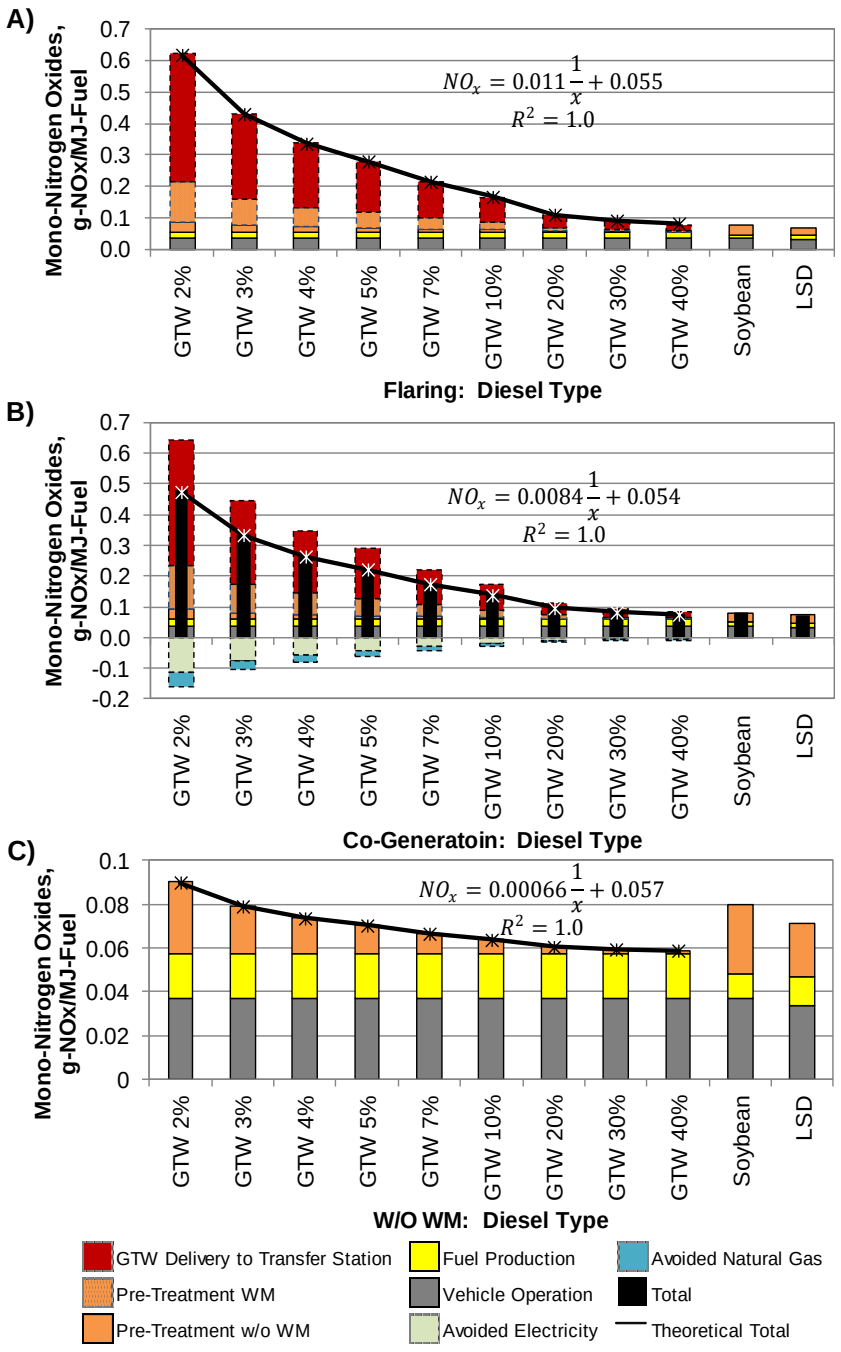


Figure C.5: Mono-nitrogen oxide complete parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD for A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total NO_x (black bar) and modeled curve (black line) are also shown.

The following tables show the NOx emissions by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.17: Landfill gas flaring scenario for mono-nitrogen oxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Mono-nitrogen Oxide, g-NOx/MJ-Fuel											
Delivery to Transfer Station	0.406	0.271	0.203	0.162	0.115	0.081	0.040	0.026	0.019	N/A	N/A
Pretreatment WM	0.128	0.084	0.062	0.049	0.035	0.023	0.010	0.006	0.004	N/A	N/A
Pretreatment w/o WM	0.033	0.022	0.017	0.013	0.009	0.007	0.003	0.002	0.002	0.032	0.025
Fuel Production	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.011	0.013
Vehicle Operation	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.033
Total	0.625	0.434	0.339	0.282	0.217	0.168	0.110	0.091	0.082	0.080	0.071
Percent Contribution, %											
Delivery to Transfer Station	65	62	60	58	53	48	36	29	24	N/A	N/A
Pretreatment WM	20	19	18	17	16	14	9	6	4	N/A	N/A
Pretreatment w/o WM	5	5	5	5	4	4	3	2	2	40	34
Fuel Production	3	5	6	7	9	12	18	22	25	14	19
Vehicle Operation	6	8	11	13	17	22	33	40	45	46	47
Reduction, %											
Compared to Soybean	684	445	325	254	172	110	39	15	3	0	-10
Compared to LSD	774	507	374	294	203	134	54	28	14	11	0

Table C.18: Landfill gas cogeneration scenario for mono-nitrogen oxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Mono-nitrogen Oxide, g-NOx/MJ-Fuel											
Delivery to Transfer Station	0.406	0.271	0.203	0.162	0.115	0.081	0.040	0.026	0.019	N/A	N/A
Pretreatment WM	0.142	0.094	0.070	0.055	0.039	0.026	0.012	0.007	0.004	N/A	N/A
Pretreatment w/o WM	0.033	0.022	0.017	0.013	0.009	0.007	0.003	0.002	0.002	0.032	0.025
Fuel Production	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.011	0.013
Vehicle Operation	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.033
Avoided Electricity	-0.112	-0.075	-0.056	-0.045	-0.032	-0.022	-0.011	-0.007	-0.006	N/A	N/A
Avoided Natural Gas	-0.048	-0.032	-0.024	-0.019	-0.014	-0.010	-0.005	-0.003	-0.002	N/A	N/A
Total	0.479	0.337	0.266	0.223	0.175	0.138	0.096	0.082	0.074	0.080	0.071
Percent Contribution, %											
Delivery to Transfer Station	85	80	76	73	66	58	42	32	26	N/A	N/A
Pretreatment WM	30	28	26	25	22	19	12	8	6	N/A	N/A
Pretreatment w/o WM	7	7	6	6	5	5	3	3	2	40	34
Fuel Production	4	6	8	9	12	15	21	25	27	14	19
Vehicle Operation	8	11	14	17	21	27	39	45	50	46	47
Avoided Electricity	-23	-22	-21	-20	-18	-16	-12	-9	-8	N/A	N/A
Avoided Natural Gas	-10	-9	-9	-9	-8	-7	-5	-4	-3	N/A	N/A
Reduction, %											
Compared to Soybean	501	323	234	180	120	74	20	2	-6	0	-10
Compared to LSD	570	371	272	212	145	93	34	14	4	11	0

Table C.19: Without GTW waste management scenario for mono-nitrogen oxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Mono-nitrogen Oxides, g-NOx/MJ-fuel											
Pretreatment	0.033	0.022	0.017	0.013	0.009	0.007	0.003	0.002	0.002	0.032	0.025
Fuel Production	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.011	0.013
Vehicle Operation	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.037	0.033
Total	0.090	0.079	0.074	0.070	0.067	0.064	0.060	0.059	0.059	0.080	0.071
Percent Contribution, %											
Pretreatment	37	28	22	19	14	10	5	4	3	40	34
Fuel Production	22	26	27	29	30	32	34	34	35	14	19
Vehicle Operation	41	47	50	52	55	58	61	62	63	46	47
Reduction, %											
Compared to Soybean	13	0	-7	-12	-16	-20	-24	-25	-26	0	-10
Compared to LSD	26	11	3	-1	-7	-11	-15	-17	-18	11	0

C.2.7. Sulfur Oxides

The sulfur oxide (SO_x) emissions were determined for the GTW-biodiesel process from 2-40% lipid content and compared to the soybean-biodiesel process and LSD process shown in Figure C.6. The soybean-biodiesel pretreatment dominates where soybean production accounts for 47% of total emissions due to the use of sulfuric acid in the production of phosphoric acid (P_2O_5) applied as a fertilizer. Soybean-biodiesel combustion does not have SO_x emissions because the feedstock/fuel does not contain sulfur.

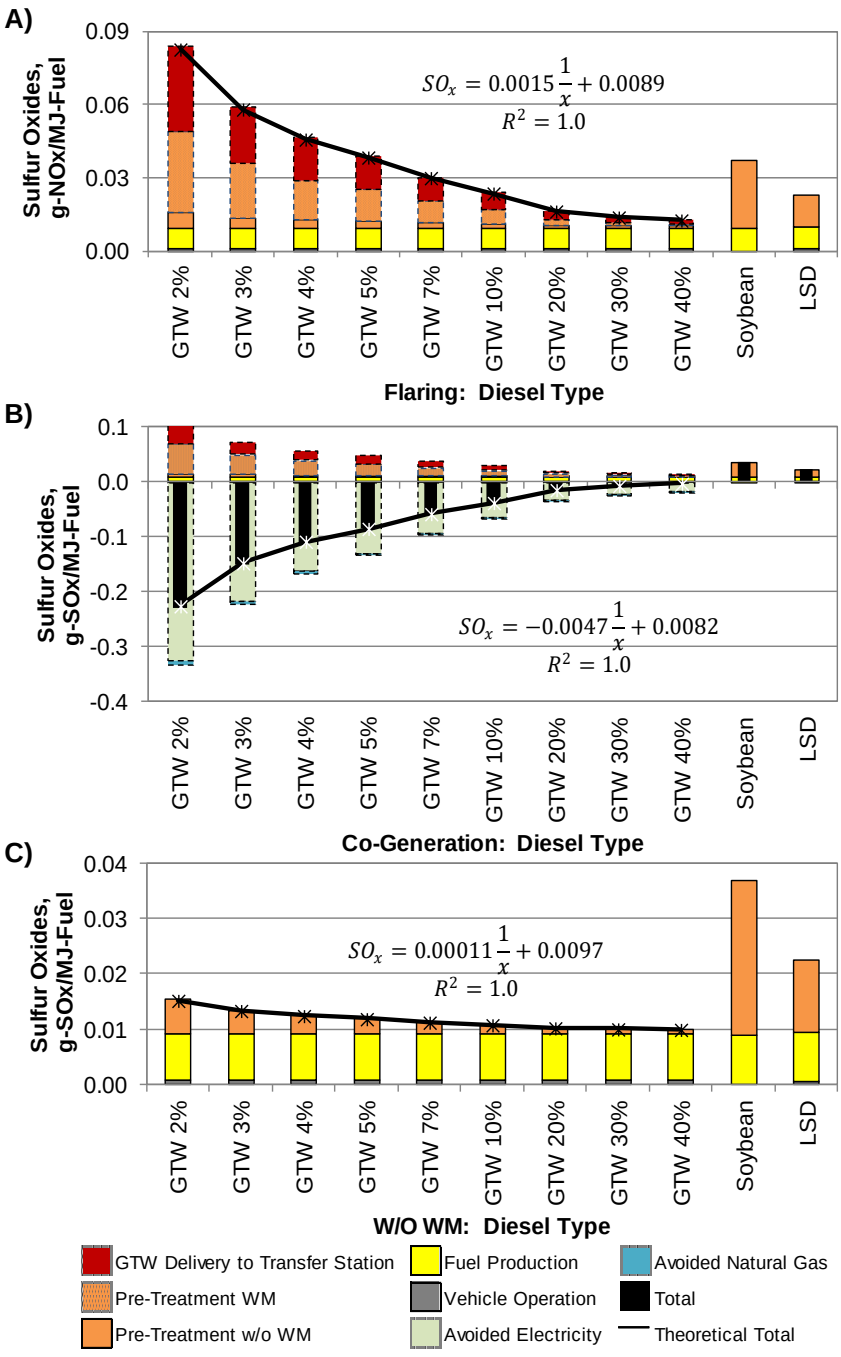


Figure C.6: Sulfur oxide complete parametric study of GTW-biodiesel compared to soybean-biodiesel and LSD for A) flaring landfill gas, B) cogeneration of landfill gas, and C) without GTW waste management. The stacked bars represent GTW-biodiesel stages: delivery of GTW to transfer station (red), pretreatment WM (orange with blue dots), pretreatment without WM (orange), fuel production (yellow), vehicle operation (gray), avoided electricity production from cogeneration (light green), and avoided natural gas from cogeneration (teal). The total SOx (black bar) and modeled curve (black line) are also shown.

The following tables show the SOx emissions by process stage, the percent contribution of each process stage, and the percent reduction compared to soybean-biodiesel and LSD for each of the waste scenarios.

Table C.20: Landfill gas flaring scenario for sulfur oxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Sulfur Oxides, g-SOx/MJ-Fuel											
Delivery to Transfer Station	0.035	0.023	0.017	0.014	0.010	0.007	0.003	0.002	0.002	N/A	N/A
Pretreatment WM	0.033	0.022	0.016	0.013	0.009	0.006	0.003	0.001	0.001	N/A	N/A
Pretreatment w/o WM	0.006	0.004	0.003	0.003	0.002	0.002	0.001	0.001	0.001	0.028	0.013
Fuel Production	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.009
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001
Total	0.084	0.059	0.046	0.039	0.030	0.024	0.016	0.014	0.012	0.037	0.022
Percent Contribution, %											
Delivery to Transfer Station	42	40	38	36	33	29	21	16	13	N/A	N/A
Pretreatment WM	40	38	35	33	30	25	16	10	6	N/A	N/A
Pretreatment w/o WM	7	7	7	7	7	7	7	7	7	76	58
Fuel Production	10	14	18	22	28	35	51	61	67	24	39
Vehicle Operation	1	1	2	2	3	3	5	6	6	0	2
Reduction, %											
Compared to Soybean	127	59	25	5	-18	-36	-56	-63	-66	0	-39
Compared to LSD	272	161	105	72	34	5	-28	-39	-45	64	0

Table C.21: Landfill gas cogeneration scenario for sulfur oxide emissions.

Lipid Content	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soybean	LSD
Sulfur Oxides, g-SOx/MJ-Fuel											
Delivery to Transfer Station	0.035	0.023	0.017	0.014	0.010	0.007	0.003	0.002	0.002	N/A	N/A
Pretreatment WM	0.054	0.036	0.026	0.021	0.015	0.010	0.005	0.003	0.002	N/A	N/A
Pretreatment w/o WM	0.006	0.004	0.003	0.003	0.002	0.002	0.001	0.001	0.001	0.028	0.013
Fuel Production	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.009
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001
Avoided Electricity	-0.325	-0.216	-0.162	-0.130	-0.093	-0.065	-0.032	-0.022	-0.016	N/A	N/A
Avoided Natural Gas	-0.008	-0.005	-0.004	-0.003	-0.002	-0.002	-0.001	-0.001	0.000	N/A	N/A
Total	-0.229	-0.150	-0.110	-0.086	-0.059	-0.039	-0.015	-0.007	-0.003	0.037	0.022
Percent Contribution, %											
Delivery to Transfer Station	-15	-15	-16	-16	-17	-18	-23	-31	-52	N/A	N/A
Pretreatment WM	-24	-24	-24	-24	-25	-26	-30	-38	-57	N/A	N/A
Pretreatment w/o WM	-3	-3	-3	-3	-4	-4	-8	-13	-27	76	58
Fuel Production	-4	-6	-8	-10	-14	-21	-55	-117	-262	24	39
Vehicle Operation	0	-1	-1	-1	-1	-2	-5	-11	-24	0	2
Avoided Electricity	142	145	147	150	157	167	216	303	510	N/A	N/A
Avoided Natural Gas	4	4	4	4	4	4	5	8	13	N/A	N/A
Reduction, %											
Compared to Soybean	-722	-507	-399	-335	-261	-205	-141	-119	-109	0	-39
Compared to LSD	-1118	-766	-590	-484	-363	-273	-167	-132	-114	64	0

Table C.22: Without GTW waste management scenario for sulfur oxide emissions.

Diesel Type	GTW 2%	GTW 3%	GTW 4%	GTW 5%	GTW 7%	GTW 10%	GTW 20%	GTW 30%	GTW 40%	Soy-bean	LSD
Sulfur Oxides, g-SOx/MJ-fuel											
Pretreatment	0.006	0.004	0.003	0.003	0.002	0.002	0.001	0.001	0.001	0.028	0.013
Fuel Production	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.009
Vehicle Operation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001
Total	0.015	0.013	0.012	0.012	0.011	0.011	0.010	0.010	0.010	0.037	0.022
Percent Contribution, %											
Pretreatment	41	32	27	24	19	16	11	10	9	76	58
Fuel Production	54	62	67	70	74	77	81	83	84	24	39
Vehicle Operation	5	6	6	6	7	7	8	8	8	0	2
Reduction, %											
Compared to Soybean	-58	-64	-66	-68	-69	-71	-72	-73	-73	0	-39
Compared to LSD	-32	-40	-44	-47	-50	-52	-54	-55	-56	64	0

C.3. Sensitivity Analysis

C.3.1. Sensitivity of Model Results to Percent FFA Composition of GTW Lipids

GTW lipid composition is also variable. In this model, the assumed free fatty acid content (%FFA) was high which was based off of initial samples of GTW lipids received in the laboratory. In the longitudinal study, the average GTW lipid content was approximately 80%FFA(Cairncross et al., 2015). Therefore, a preliminary analysis was performed to determine the change in GWP_{100}. GTW lipids composition was assumed to be 80% oleic acid and 20% triolein. The triolein was not reacted into biodiesel since the process model does not include transesterification. The triolein remains as the residual co-product, "bio-bunker," in the distillation process. The life cycle inventory was updated for this process and GWP_{100} was determined. Lipid contents of 5% and 30%

containing 80%FFA were compared to the consequential LCA approach for 5% and 30% lipid contents shown in Table C.23.

Table C.23: Comparison of predicted GWP_{100} from consequential LCA for low FFA GTW-biodiesel process and high FFA GTW-biodiesel process.

	GWP_{100} from Low FFA Scenario		GWP_{100} from High FFA Scenario		Ratio of Low FFA to High FFA	
	5% Lipids	30% Lipids	5% Lipids	30% Lipids	5% Lipids	30% Lipids
Pretreatment	15.2	2.4	12.5	2.0	1.2	1.2
Fuel Production	16.5	16.5	14.2	14.2	1.2	1.2
Vehicle Operation	4.8	4.8	4.8	4.8	1.0	1.0
Total	36.4	23.7	31.5	21.0	1.2	1.1

The lower FFA did not increase the GWP_{100} significantly for either 5% or 30% lipid contents. The effect of FFA on GWP_{100} is similar to the effect of overall lipid content: the lower the FFA, the higher the GWP_{100}. The lower FFA is equivalent to having a lower lipid content. For example the 5% lipid content with 80% FFA GWP_{100} is the same as 3.5% lipid content with 95% FFA GWP_{100}.

C.3.2. Sensitivity to GTW Composition and Monte Carlo Simulation

The Monte Carlo simulation was performed to determine GWP_{100} of both the attributional and consequential LCA approaches for the GTW-biodiesel process. Two lognormal distributions were used based off of raw GTW lipid contents and dewatered GTW lipid contents. The attributional LCA approach included two scenarios based off of landfill gas flaring and cogeneration of landfill gas. The consequential LCA approach omits the impacts associated with GTW waste management and the delivery of GTW to

the transfer station because they are nearly the same in the current GTW handling process and the proposed GTW-biodiesel process.

C.3.2.1. Longitudinal Study

The longitudinal study occurred between June 2014 and June 2015. A 500 gal tank was located at a transfer station in New Jersey. The GTW hauler deposited interior grease trap collections into the tank. The GTW typically settled into three layers: (1) floating solids with extractable lipids, (2) wastewater, and (3) sediments. Each layer width was measured and knowing the diameter of the tank, the volume was estimated. The top floating layer was sampled and heated to remove the lipids. The lipid percent was determined as a percent of the total tank volume (lipids from raw GTW) and as a percent of the floating solids layer (lipids from settled GTW float grease or dewatered GTW). The histogram below depicts the frequency of lipid percentages found throughout the longitudinal study.

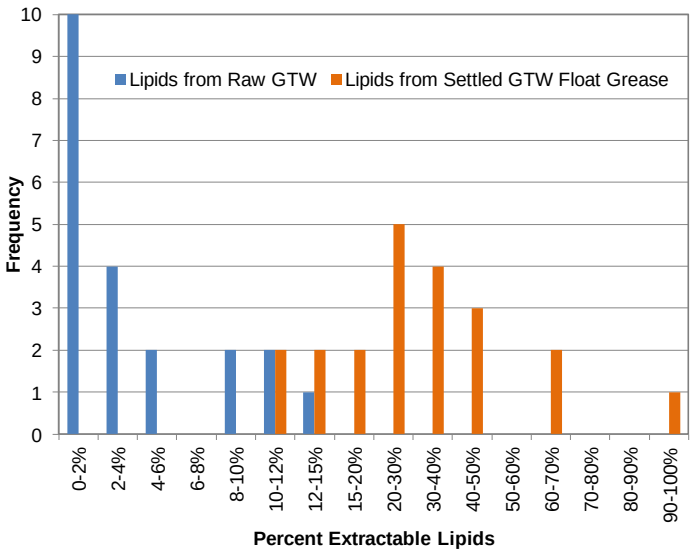


Figure C.7: Histogram of lipid contents as a percentage of raw GTW (blue) and as a percentage of settled GTW float grease (orange).

The data of each raw GTW lipid content and dewatered was fit to a lognormal distribution using Oracle Crystal Ball. The cumulative distributions for the lipid contents are shown in Figure C.8.

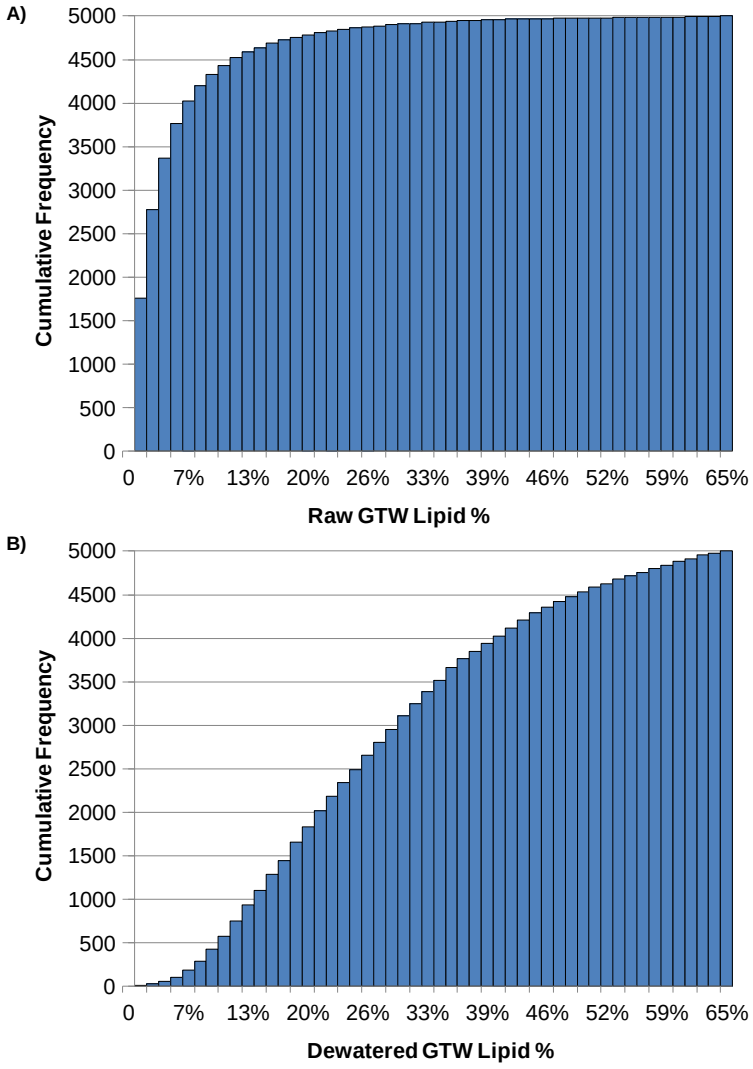


Figure C.8: Cumulative distributions for lipid content (as a mass fraction) used in the Monte Carlo simulation for (A) raw GTW and (B) dewatered GTW.

The cumulative distribution for the raw GTW had a faster rate than the dewatered GTW as the median was 2% lipids and 27% for raw GTW and dewatered GTW,

respectively. 90% confidence for the raw GTW distribution was 11% lipid content; lipid concentrations less than 10% were shown to have larger environmental impacts. This result emphasizes the need for GTW dewatering since the lipids are concentrated and result in higher lipid contents and therefore lower environmental impacts.

C.3.2.2. Model Fitting Data

The environmental impacts were estimated by using the equation derived for the model fitting and using the distribution of the lipid contents.

The "Total Eqn 4.11" in the following tables was calculated using the equation 4.11 from Section 4.2.6 below:

$$\frac{I_{Total}}{E_{Biodiesel}} = \left(\frac{\hat{I}_{PT}}{\phi \Delta \widehat{H}_c}\right)\frac{1}{x} + \left(\frac{\hat{I}_{FP}}{\phi \Delta \widehat{H}_c} + \frac{\hat{I}_{VO}}{\Delta \widehat{H}_c}\right) \qquad (Eq.\,4.11)$$

Where,

$\hat{I}_i$ = environmental impact intensity of process stage i per unit mass of input (PT = pre-treatment, FP = fuel production, and VO = vehicle operation: combustion emissions)

$\Delta\hat{H}_C$ = heat of combustion of biodiesel (lower heating value, MJ/kg)

Φ = yield of fuel production process

x = lipid content

$E_{Biodiesel}$ = energy content of biodiesel produced

The first set of parenthesis in Eq. 4.11 represents the slope of the line and the second set of parenthesis represents the intercept used for the simplified equation. A summary of the slope and intercept for each scenario used for the Monte Carlo analysis is shown in Table C.24. The slope and intercept were calculated using Microsoft Excel's slope and intercept functions using y=Total impact and x=1/lipid content

Table C.24: Equation slope and intercept for model fitting.

	Flaring		Cogeneration		w/o WM	
	slope	intercept	slope	intercept	slope	intercept
GWP_{100}	4.1	18	2.8	18	0.6	19
CED	0.028	0.28	0.014	0.28	0.010	0.28
CO	0.0026	0.075	0.0025	0.075	0.00042	0.075012
PM	0.00068	0.0033	0.00018	0.0033	0.000035	0.0036
NO_x	0.011	0.055	0.0084	0.054	0.00066	0.057
SO_x	0.0015	0.0089	-0.0047	0.0082	0.00011	0.0097

The following tables show the environmental impacts of the GTW-biodiesel biodiesel production for each landfill scenario by process stage over the 2-40% lipid content range. These tables were used to determine the slope and intercepts for the simplified equations.

Table C.25: GWP_{100} model fitting data.

	x (vol)	2%	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	**50.00**	**33.33**	**25.00**	**20.00**	**14.29**	**10.00**	**5.00**	**3.33**	**2.50**
	1/x (mass)	**55.98**	**37.26**	**27.93**	**22.32**	**15.91**	**11.10**	**5.49**	**3.61**	**2.68**
	kg GTW	**1.44**	**0.96**	**0.72**	**0.57**	**0.41**	**0.29**	**0.14**	**0.09**	**0.07**
Flare	IPT Flare	207	137	103	82	58	40	20	13	9
	Total	226	156	122	101	77	59	39	32	28
	Total Eq. 4.11	226	156	122	101	77	59	39	32	28
	Theoretical Total (slope*1/x+intercept)	223	155	121	100	77	59	39	32	29
Co-Gen	IPT Cogeneration	143	95	71	57	40	28	13	8	6
	Total	162	114	90	76	59	47	32	27	25
	Total Eq. 4.11	162	114	90	76	59	47	32	27	25
	Theoretical Total (slope*1/x+intercept)	161	113	89	75	59	47	32	28	25
W/O WM	IPT w/o WM	31	21	16	13	9	6	3	2	1
	Total	50	40	35	31	28	25	22	21	20
	Total Eq. 4.11	50	40	35	31	28	25	22	21	20
	Theoretical Total (slope*1/x+intercept)	50	40	34	31	28	25	22	21	20

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	14.19	4.79

Table C.26: Fossil CED model fitting data.

	x (vol)	2%	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	50.00	33.33	25.00	20.00	14.29	10.00	5.00	3.33	2.50
	1/x (mass)	55.98	37.26	27.93	22.32	15.91	11.10	5.49	3.61	2.68
	kg GTW	1.44	0.96	0.72	0.57	0.41	0.29	0.14	0.09	0.07
Flare	IPT Flare	1.43	0.95	0.71	0.57	0.40	0.28	0.14	0.09	0.06
	Total	1.72	1.24	1.00	0.85	0.69	0.56	0.42	0.37	0.35
	Total Eq. 4.11	1.71	1.23	0.99	0.84	0.68	0.56	0.41	0.36	0.34
	Theoretical Total (slope*1/x+intercept)	1.70	1.23	0.99	0.85	0.68	0.56	0.42	0.37	0.35
Co-Gen	IPT Cogeneration	0.70	0.46	0.34	0.27	0.19	0.13	0.06	0.04	0.03
	Total	0.98	0.74	0.63	0.56	0.48	0.42	0.35	0.32	0.31
	Total Eq. 4.11	0.97	0.74	0.62	0.55	0.47	0.41	0.34	0.31	0.30
	Theoretical Total (slope*1/x+intercept)	0.97	0.74	0.62	0.55	0.48	0.42	0.35	0.32	0.31
W/O WM	IPT w/o WM	0.51	0.34	0.25	0.20	0.14	0.10	0.05	0.03	0.02
	Total	0.79	0.62	0.54	0.48	0.43	0.38	0.33	0.32	0.31
	Total Eq. 4.11	0.78	0.61	0.53	0.48	0.42	0.37	0.32	0.31	0.30
	Theoretical Total (slope*1/x+intercept)	0.78	0.62	0.53	0.48	0.43	0.38	0.33	0.32	0.31

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	0.28	0.00

Table C.27: Carbon monoxide model fitting data.

	x (vol)	2%	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	50.00	33.33	25.00	20.00	14.29	10.00	5.00	3.33	2.50
	1/x (mass)	55.98	37.26	27.93	22.32	15.91	11.10	5.49	3.61	2.68
	kg GTW	1.44	0.96	0.72	0.57	0.41	0.29	0.14	0.09	0.07
Flare	IPT Flare	0.131	0.087	0.065	0.052	0.037	0.026	0.013	0.008	0.006
	Total	0.206	0.162	0.140	0.127	0.112	0.101	0.088	0.083	0.081
	Total Eq. 4.11	0.206	0.162	0.140	0.127	0.112	0.100	0.087	0.083	0.081
	Theoretical Total (slope*1/x+intercept)	0.204	0.161	0.140	0.127	0.112	0.101	0.088	0.083	0.081
Co-Gen	IPT Cogeneration	0.128	0.445	0.333	0.266	0.190	0.132	0.065	0.043	0.032
	Total	0.203	0.160	0.139	0.126	0.111	0.100	0.087	0.083	0.081
	Total Eq. 4.11	0.203	0.519	0.408	0.341	0.264	0.207	0.140	0.118	0.106
	Theoretical Total (slope*1/x+intercept)	0.202	0.159	0.138	0.125	0.111	0.100	0.087	0.083	0.081
W/O WM	IPT w/o WM	0.021	0.014	0.011	0.008	0.006	0.004	0.002	0.001	0.001
	Total	0.096	0.089	0.086	0.083	0.081	0.079	0.077	0.076	0.076
	Total Eq. 4.11	0.096	0.089	0.085	0.083	0.081	0.079	0.077	0.076	0.076
	Theoretical Total (slope*1/x+intercept)	0.096	0.089	0.086	0.083	0.081	0.079	0.077	0.076	0.076

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	0.009	0.066

Table C.28: Particulate matter model fitting data.

	x (vol)	2%	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	50.00	33.33	25.00	20.00	14.29	10.00	5.00	3.33	2.50
	1/x (mass)	55.98	37.26	27.93	22.32	15.91	11.10	5.49	3.61	2.68
	kg GTW	1.44	0.96	0.72	0.57	0.41	0.29	0.14	0.09	0.07
Flare	IPT Flare	0.034	0.023	0.017	0.014	0.010	0.007	0.003	0.002	0.001
	Total	0.038	0.026	0.021	0.017	0.013	0.010	0.007	0.006	0.005
	Total Eq. 4.11	0.038	0.026	0.020	0.017	0.013	0.010	0.007	0.005	0.005
	Theoretical Total (slope*1/x+intercept)	0.037	0.026	0.020	0.017	0.013	0.010	0.007	0.006	0.005
Co-Gen	IPT Cogeneration	0.009	0.406	0.304	0.243	0.173	0.121	0.060	0.039	0.029
	Total	0.012	0.009	0.008	0.007	0.006	0.005	0.004	0.004	0.004
	Total Eq. 4.11	0.012	0.409	0.307	0.246	0.176	0.124	0.063	0.043	0.032
	Theoretical Total (slope*1/x+intercept)	0.012	0.009	0.008	0.007	0.006	0.005	0.004	0.004	0.004
W/O WM	IPT w/o WM	0.002	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000
	Total	0.005	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004
	Total Eq. 4.11	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004	0.004
	Theoretical Total (slope*1/x+intercept)	0.005	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	0.002	0.001

Table C.29: Mono-nitrogen oxides model fitting data.

	x (vol)	0.02	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	50	33.33	25.00	20.00	14.29	10.00	5.00	3.33	2.50
	1/x (mass)	55.9805	37.26	27.93	22.32	15.91	11.10	5.49	3.61	2.68
	kg GTW	1.4387	0.96	0.72	0.57	0.41	0.29	0.14	0.09	0.07
Flare	IPT Flare	0.567	0.377	0.282	0.224	0.160	0.110	0.053	0.034	0.025
	Total	0.625	0.434	0.339	0.282	0.217	0.168	0.110	0.091	0.082
	Total Eq. 4.11	0.624	0.434	0.338	0.281	0.216	0.167	0.110	0.091	0.081
	Theoretical Total (slope*1/x+intercept)	0.618	0.430	0.336	0.280	0.216	0.167	0.111	0.092	0.083
Co-Gen	IPT Cogeneration	0.422	0.421	0.315	0.251	0.178	0.123	0.059	0.038	0.028
	Total	0.479	0.337	0.266	0.223	0.175	0.138	0.096	0.082	0.074
	Total Eq. 4.11	0.478	0.478	0.371	0.308	0.235	0.180	0.116	0.095	0.084
	Theoretical Total (slope*1/x+intercept)	0.474	0.334	0.264	0.222	0.174	0.138	0.096	0.082	0.075
W/O WM	IPT w/o WM	0.033	0.022	0.017	0.013	0.009	0.007	0.003	0.002	0.002
	Total	0.090	0.079	0.074	0.070	0.067	0.064	0.060	0.059	0.059
	Total Eq. 4.11	0.090	0.079	0.073	0.070	0.066	0.063	0.060	0.059	0.058
	Theoretical Total (slope*1/x+intercept)	0.090	0.079	0.074	0.070	0.067	0.064	0.060	0.059	0.059

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	0.02	0.04

Table C.30: Sulfur oxide model fitting data.

	x (vol)	0.02	3%	4%	5%	7%	10%	20%	30%	40%
	1/x (vol)	50	33.33	25.00	20.00	14.29	10.00	5.00	3.33	2.50
	1/x (mass)	55.9805	37.26	27.93	22.32	15.91	11.10	5.49	3.61	2.68
	kg GTW	1.4387	0.96	0.72	0.57	0.41	0.29	0.14	0.09	0.07
Flare	IPT Flare	0.074	0.050	0.037	0.030	0.021	0.015	0.007	0.005	0.003
	Total	0.084	0.059	0.046	0.039	0.030	0.024	0.016	0.014	0.012
	Total Eq. 4.11	0.083	0.058	0.046	0.038	0.030	0.023	0.016	0.013	0.012
	Theoretical Total (slope*1/x+intercept)	0.083	0.058	0.046	0.038	0.030	0.024	0.016	0.014	0.013
Co-Gen	IPT Cogeneration	-0.238	0.230	0.172	0.138	0.098	0.068	0.033	0.022	0.016
	Total	-0.229	-0.150	-0.110	-0.086	-0.059	-0.039	-0.015	-0.007	-0.003
	Total Eq. 4.11	-0.229	0.239	0.181	0.146	0.107	0.077	0.042	0.030	0.025
	Theoretical Total (slope*1/x+intercept)	-0.226	-0.148	-0.109	-0.086	-0.059	-0.039	-0.015	-0.007	-0.004
W/O WM	IPT w/o WM	0.006	0.004	0.003	0.003	0.002	0.002	0.001	0.001	0.001
	Total	0.015	0.013	0.012	0.012	0.011	0.011	0.010	0.010	0.010
	Total Eq. 4.11	0.015	0.013	0.012	0.012	0.011	0.011	0.010	0.010	0.010
	Theoretical Total (slope*1/x+intercept)	0.015	0.013	0.012	0.012	0.011	0.011	0.010	0.010	0.010

Density GTW (kg/L)	phi	IFP	IVO
1.11	1.03	0.008	0.001

Appendix D. Techno-economic Analysis and Life Cycle Assessment

D.1. Landfill Emissions Equations

The landfill methane emissions were determined by using the landfill emission carbon balance shown in Figure D.1 found in the Swedish landfill emission report (Sundqvist, 1999).

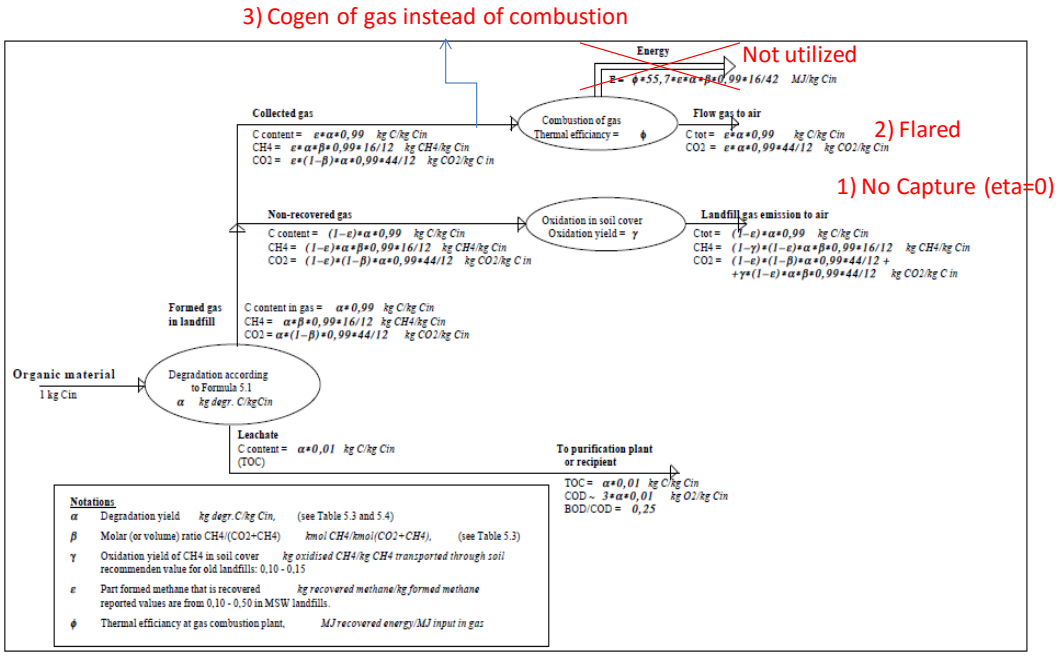


Figure 5.5. Carbon balance of a MSW landfill. The factors α, β, γ, ϕ, and ε are described in Table 5.3 and 5.4 and in the text.

Figure D.1: Landfill flow diagram to estimate landfill gas emissions.

The variables alapha, beta, gamma, and epsilon used in the analysis are shown in Table D.1.

Table D.1: Landfill parameters to determine methane emissions.

Parameter	Symbol	Unit	Biofuel Production	Business as Usual
Degradation yield	α	kgdegC/kgCin	75%	86%
Molar ratio of CH_4 in gas	β	$CH_4/(CO_2+CH_4)$	50%	61%
Oxidation yield of CH_4 in soil cover	γ	kg oxidized CH_4/kg CH_4 transported through soil	**15%**	**15%**
Recovered CH_4	ε	kg CH_4 recovered/kg CH_4 formed	**75%**	**75%**

The bold values represent parameters that are variable and have fitted distributions. Gamma had a range between 40-60% oxidation depending on the soil thickness, soil type, and climate (Spokas et al., 2011). The recovered methane was fit to a triangular distribution with an average of 75% and a range of 50-95% (USEPA, 2015b).

D.2. Data Fitting

D.2.1. Grease Trap Waste Data Fitting

For the GTW FFA content data, the multiple distributions were considered adequate fits according to the Oracle crystal ball distribution fitting function. Therefore, when multiple distribution types were possible, the each distribution was chosen and Monte Carlo simulation was performed to choose 10,000 random data points along the distribution. This was repeated 3 times to determine the variability of each simulation run. A box plot was then made and compared to the longitudinal study data to determine which distribution type best represented the longitudinal data (Figure D.2).

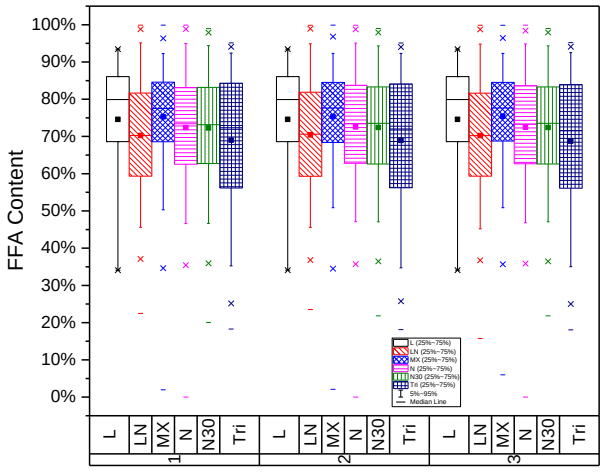


Figure D.2: GTW data fitting to longitudinal study data (L) for FFA content. MX represents data fit to a min extreme distribution, N represents data fit to a normal distribution, N30 represents data fit to a normal distribution with lower truncation at 30% and Tri represents data fit to a triangular distribution. The box represents 25-75 percentiles, whiskers represent 5-95 percentiles, the filled square represents the mean, the horizontal line within the box represents the median, the x represents the 1-99 percentiles, and the dashes represent the minimum and maximum.

The minimum extreme distribution (MX) was chosen to represent the longitudinal study (L) data because it consistently had the most similar statistical properties than the other distributions. The box and upper whiskers were closest to the longitudinal study data. The lower whiskers were not as close, but the only other distribution that showed similarity to the longitudinal study data was the triangular distribution (Tri). The statistical properties (mean, median, and the box) of the triangular distribution were not representative of the longitudinal study so despite its lower FFA whisker similarity to the longitudinal data, it was not as good a fit compared to the other distributions. While the lower whisker of the MX was not as low as the longitudinal study, the lower range of the 1-99 percentile (lower x) was matching to that of the longitudinal study.

Figure D.3displays the effect of accumulation on the range of the lipid content.

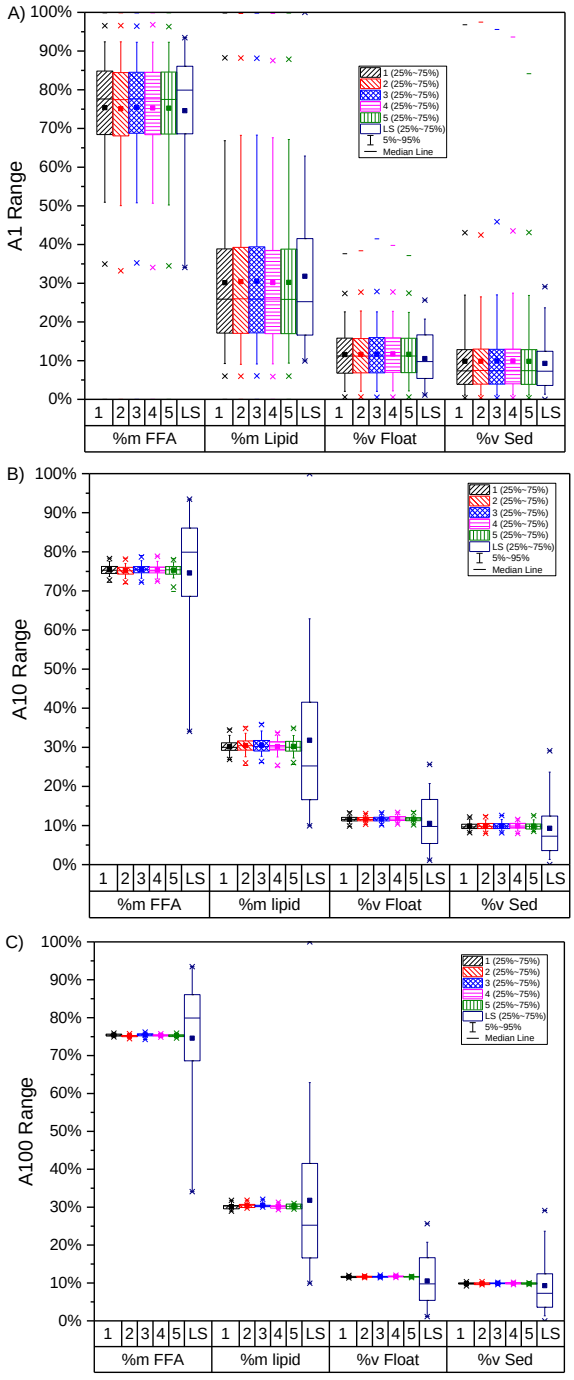


Figure D.3: Repeatability of simulations for raw GTW compared to longitudinal study (LS). 1-5 represent trials of 10,000 randomly chosen values over the fitted distribution. Boxes represent 25-75 percentiles, whiskers represent the 10-90 percentiles, x represents 1-99 percentiles, - represents minimum and maximum, the middle line represents the median, and the filled square represents the mean.

The GTW longitudinal data fitted distributions represent one truck load (500 gal settling tank) of collected waste (A1). However, at a biodiesel production plant, the raw grease would be accumulated prior to the lipid extraction. With accumulation, the range of the composition variability should decrease. Therefore, 5-10,000 trials of the composition distributions were run and two data sets were created: (A10) average of every 10 data points and (A100) average of every 100 data points. These sets of data represent an accumulation of 10 trucks and 100 trucks.

D.2.2. Grease Trap Waste Data Fitting

Choosing the distribution was sometimes difficult because multiple distribution types were considered adequate fits according to the Oracle crystal ball distribution fitting function. Therefore, when multiple distribution types were possible, the each distribution was chosen and Monte Carlo simulation was performed to choose 10,000 random data points along the distribution. A box plot was then made and compared to the longitudinal study data to determine which distribution type best represented the longitudinal data (Figure D.4).

For the cool season waste solids (Figure D.4-A), the normal distribution (N) was chosen because the box and whiskers were similar to the longitudinal study data (L) and the lower x of the normal (1 percentile) of the normal distribution was best representative of the longitudinal data. For the cool season FFA content (Figure D.4-B), the minimum extreme distribution (MX) was chosen. The box, whiskers, mean, and median were similar to the longitudinal study data for the MX distribution. The lower whisker range was around 60%m FFA for the MX compared to the 40%m FFA of the LS.

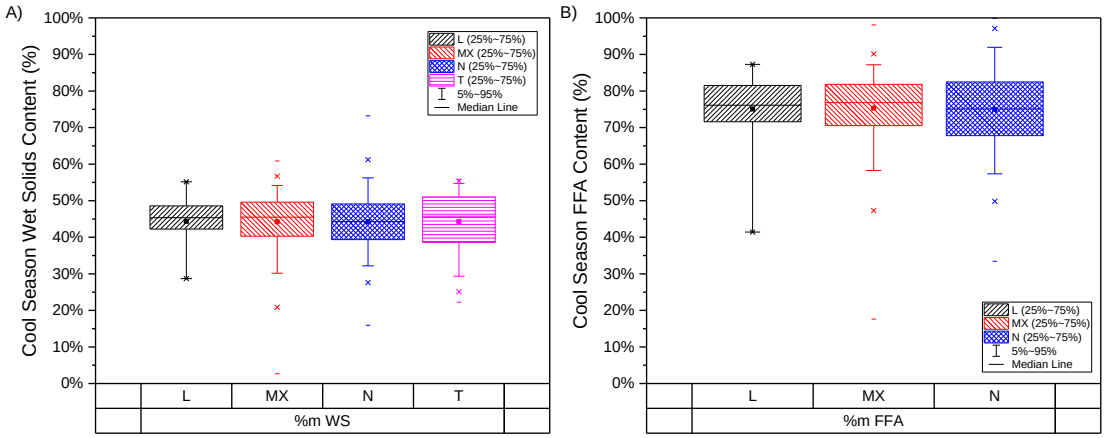


Figure D.4: Cool season data fitting to longitudinal study data (L) for A) wet solids and B) FFA content. MX represents data fit to a min extreme distribution, N represents data fit to a normal distribution, and T represents data fit to a triangular distribution. The box represents 25-75 percentiles, whiskers represent 5-95 percentiles, the filled square represents the mean, the horizontal line within the box represents the median, the x represents the 1-99 percentiles, and the dashes represent the minimum and maximum.

There were only two data points in the longitudinal study at the low range lipid content and did not occur often. While the lower whisker does not match exactly, the lower end of the 1-99 percentile (bottom x) of the MX distribution was approximately 45%m FFA and the minimum is 20% mFFA, so low FFA occurrences will be chosen in the simulation. These occasional low FFA contents in the MX distribution are more representative of the longitudinal study as compared to the normal distribution (N) that does not represent low FFA contents as well as the MX distribution.

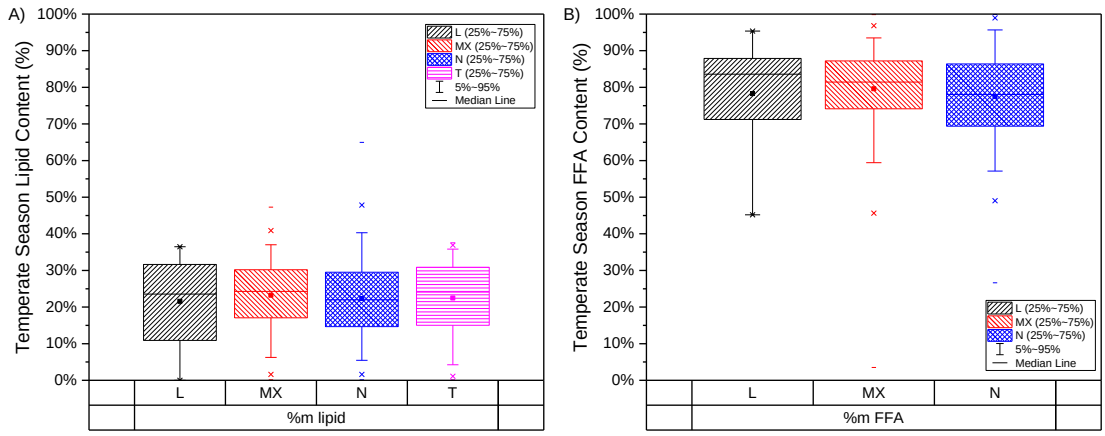


Figure D.5: Temperate season data fitting to longitudinal study data (L) for A) wet solids and B) FFA content. MX represents data fit to a min extreme distribution, N represents data fit to a normal distribution, and T represents data fit to a triangular distribution. The box represents 25-75 percentiles, whiskers represent 5-95 percentiles, the filled square represents the mean, the horizontal line within the box represents the median, the x represents the 1-99 percentiles, and the dashes represent the minimum and maximum.

For the temperate season lipid content (Figure D.5-A), the triangular distribution (T) was chosen because the range from minimum to maximum and the shape of the box were the closest to the longitudinal study data (L) than the other fitted distributions. For the temperate season FFA content (Figure D.5-B), the normal distribution (N) was chosen because its statistical properties best matched the longitudinal study data (L) compared to the minimum extreme distribution (MX). The MX distribution had minimum of approximately 5%m FFA content which has never been observed in the laboratory.

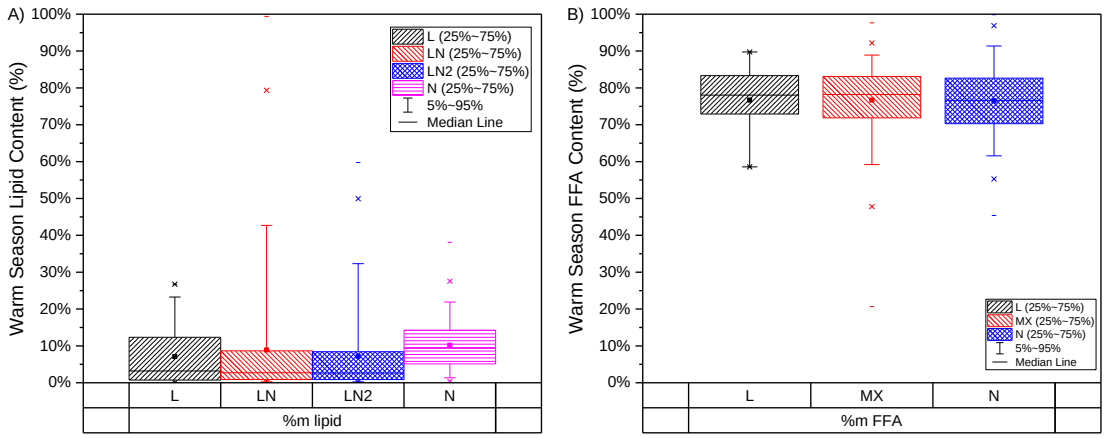


Figure D.6: Warm season data fitting to longitudinal study data (L) for A) wet solids and B) FFA content. MX represents data fit to a min extreme distribution, N represents data fit to a normal distribution, and LN represents data fit to a lognormal distribution. The box represents 25-75 percentiles, whiskers represent 5-95 percentiles, the filled square represents the mean, the horizontal line within the box represents the median, the x represents the 1-99 percentiles, and the dashes represent the minimum and maximum.

For the warm season lipid content (Figure D.6-A), the second lognormal distribution (LN2) was chosen. The highest lipid content during the warm season was 30%m lipids. The normal distribution (N) closely resembled the longitudinal study data (LS) in the higher lipid contents; however, it did not represent the low lipid contents well. The most prominent result of the longitudinal study was that there was extremely low lipid content in the warm season compared to the other seasons; therefore, it is important to get the best fit at the lower range of lipid contents. The problem with the first lognormal distribution was that when the range was 0.15%-99.9%, the 1-99% range was extended up to 80%m lipids which were rare even in the winter season when the most lipids are able to be extracted. In order to best represent the LS data, the LN distribution was truncated to 60%m lipids.

D.3. Biodiesel Production

The annual production of biodiesel for GTW and SSG is shown in Figure D.7.

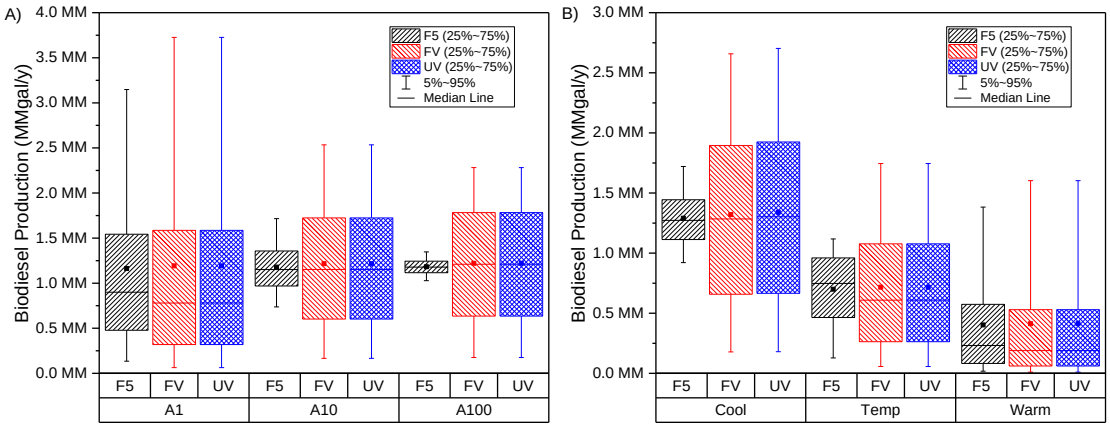


Figure D.7: Annual biodiesel production from A) non-aggregated GTW (A1) and aggregated GTW (A10 and A100) and B) SSG during cool, temperate, and warm seasons. Plant capacity studied fixed plant size at fixed 5,000 gal/h flow rate for GTW and 500 gal/h flow rate for SSG (F5), fixed plant capacity with a variable flow rate (FV), and unfixed plant capacity with variable flow rate (UV).

The average amount of GTW biodiesel production was the same as SSG production in the winter (if the winter season were to last an entire year). The flow rate of GTW was 10 times that of SSG; however, since SSG did not need ambient settling (it was considered to have a float volume of 99%), the amount of brown grease available was the same. The effect of the flow rate can be seen between the two variable scenarios (FV and UV) and the F5. The F5 represents biodiesel production and its variability solely due to the raw grease composition.

Appendix E. Life Cycle Impact Analysis for The Production of Five Theses

The greenhouse gas (GHG) emissions associated with the production of five copies of this thesis was performed using a life cycle impact assessment (LCIA). Figure E.1 displays system boudnary, inventory, and results for the process. The writing required the use of a laptop, two networks for internet usage. The estimated amount of usage was approximated to 540 h but was normalized by the total number of theses. The printing process included paper delivery from a warehouse 60 mi away and an estimated 10.5 kg of paper. Coffee was not included in the process because it would have been consumed regardless of thesis production.

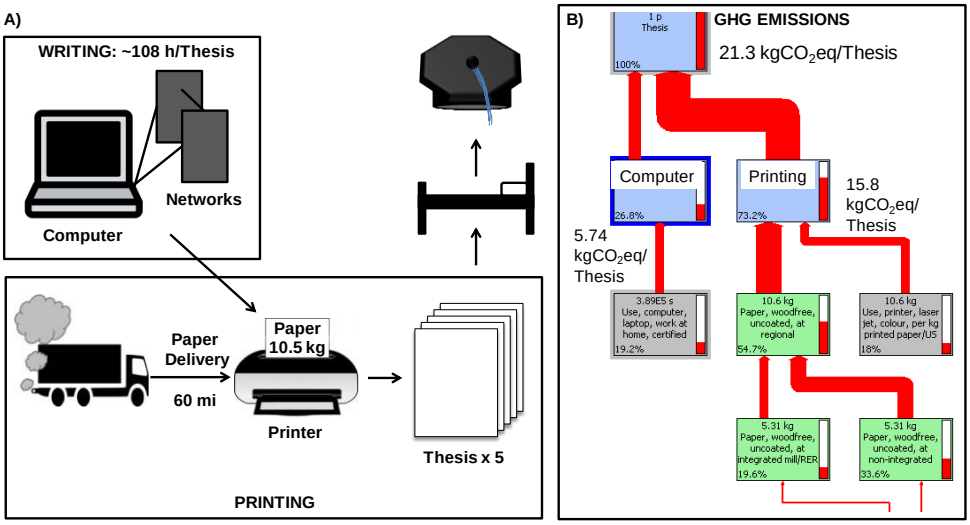


Figure E.1: LCIA for Thesis Production: (A) System Boundary and Inventory and (B) GHG Emissions

The GHG emissions were estimated using the SimaPro Ecoinvent database and the100-y global warming potential. Results show that the the GHG emissions are 21.3 kgCO2/Thesis. Printing has the highest contribution at 73% of total GHG emission or about 1.5 $kgCO_2$/kgPaper.

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Vita

Megan E. Hums was born and raised in Reading, Pennsylvania. She graduated high school in 2007 and began her undergraduate studies in Chemical Engineering at Widener University. While attending Widener, Megan was active in multiple organizations including being a founding member of the Widener Chapter of Alpha Chi Sigma and Engineers Without Borders. As a member of Engineers Without Borders, Megan had the privilege of traveling on two assessment trips to Ella Drua, Panama to research the feasibility of supplying solar electricity to the small, rural village. Megan was also enrolled in the co-op program at Widener and gained work experience as a process engineer at DuPont and Johnson Matthey. She decided to take the fundamentals of engineering exam and passed in 2010. In spring of 2011, Megan completed her B.S. with honors in Chemical Engineering and a minor in Chemistry.

Because of her interest in learning and renewable energy, Megan joined the PhD program in Chemical Engineering at Drexel University in the fall of 2011. Under the guidance of Dr. Richard Cairncross and Dr. Sabrina Spatari, Megan has enjoyed her duties as a research assistant in evaluating the environmental impacts of and producing biodiesel from wastewater greases, despite working with one of more malodorous of feedstocks. Megan had the honor in serving as research assistant and primary investigator for Environmental Fuel Research, LLC during a phase I EPA SBIR grant. As this chapter in her life comes to an end, Megan is looking to continue research in resource recovery.